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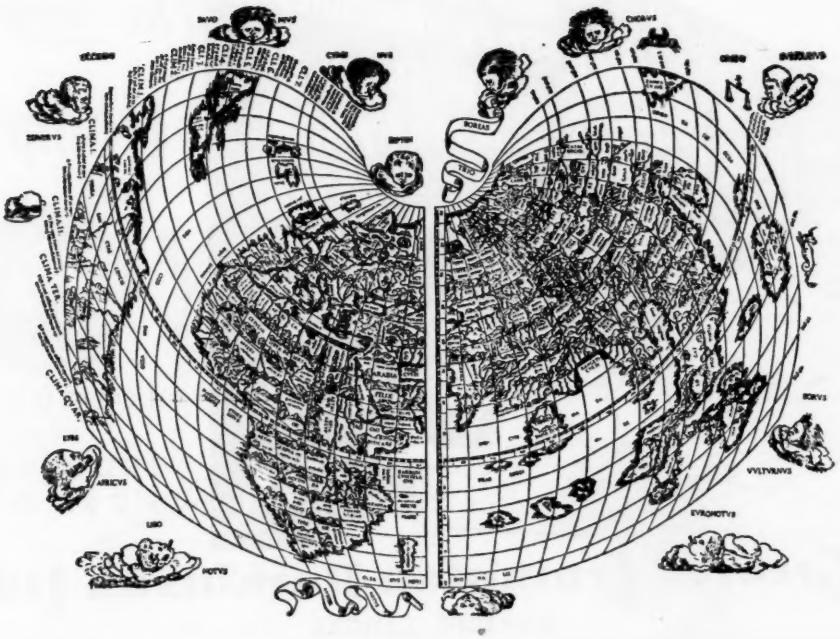

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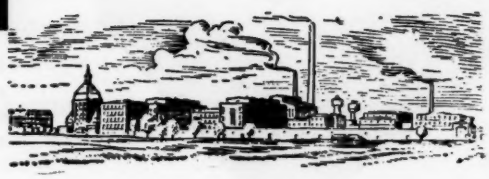

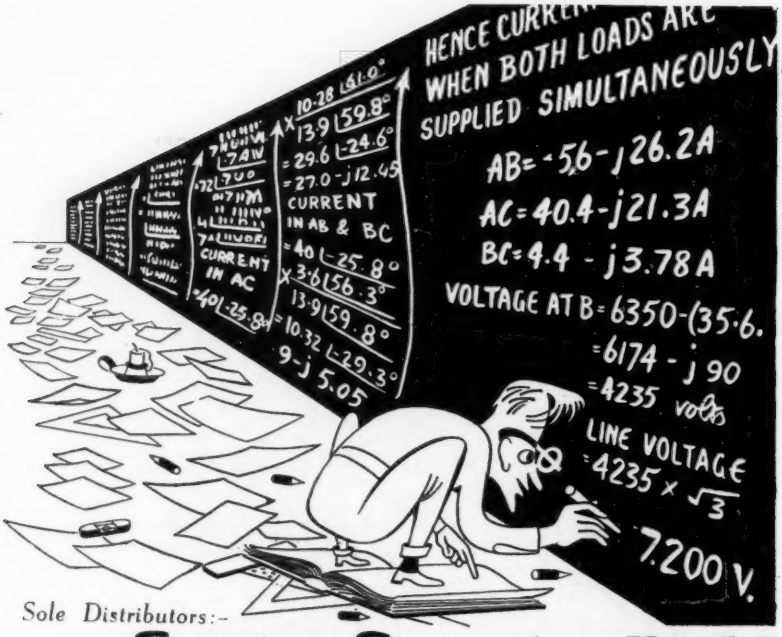
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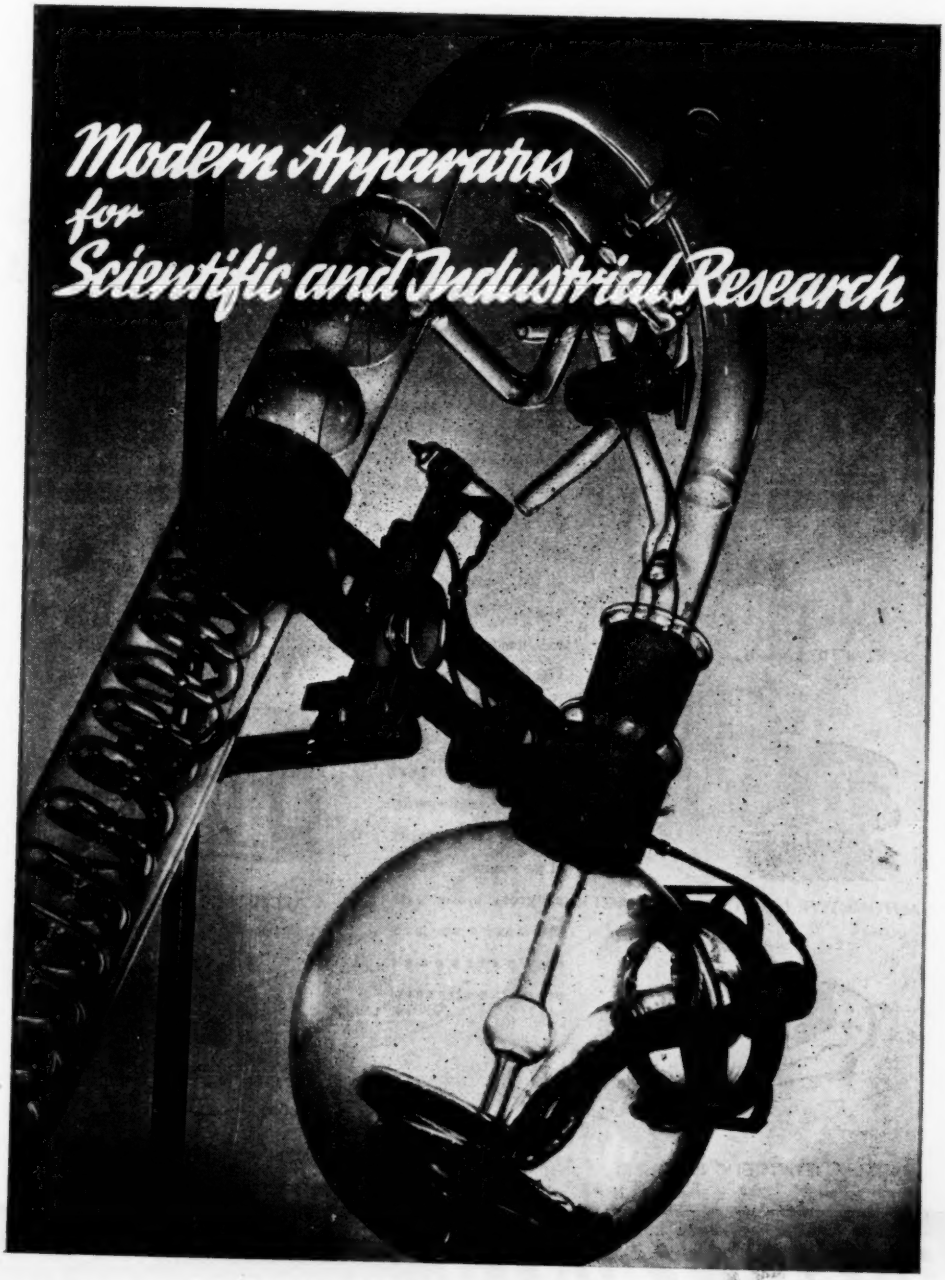

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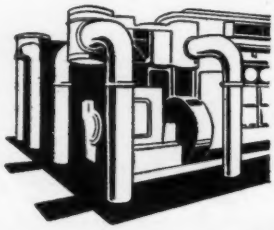

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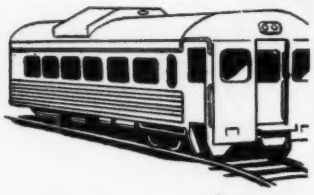

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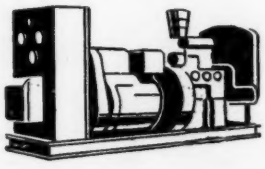

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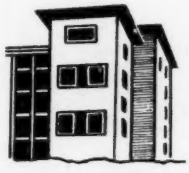

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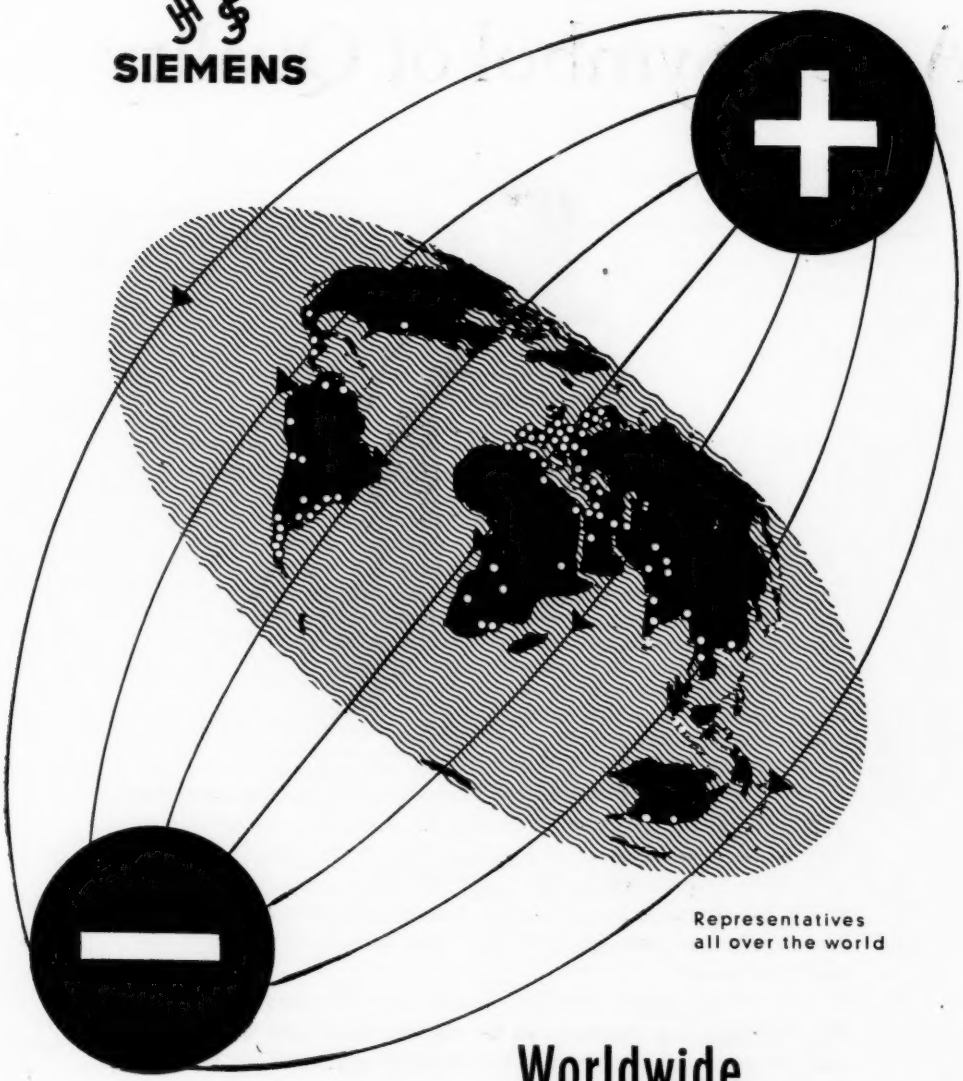

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Foreword

Recognising the importance of scientific research in the industrial development and prosperity of a country, the Government of Pakistan took early steps to build up the industrial research organisation of the country, and the creation of the Department of Scientific and Industrial Research in 1949 under the Ministry of Industries was the first step in this direction. As a result of the activities of this Department, the constitution of the Council of Scientific and Industrial Research was drawn up with due reference to the structure of the organisation in the pre-Independence period, and to the special needs and requirements of the greatly changed situation in Pakistan, and the Council was established as an autonomous body in April, 1953.

The functions of the Council cover a wide range of activities generally directed towards the promotion and fostering of scientific research having a bearing on the industrial development of the country, and the utilization of its natural resources to the best economic advantage. While the scope of the activities of the Council has been kept broad and comprehensive, due priority is given to problems which are of importance to the immediate needs of the country. In the pursuit of such a programme, however, it is generally recognised that, if science is to get a chance of effectively promoting the industrial development of the country, laboratory investigations in both pure and applied fields, followed by research development work on a pilot plant scale, will all have to come under the purview of the Council's activities.

By far the most important among the aims and objects of the Council was the establishment of National Laboratories in the two wings of the country. On the recommendations of a planning committee constituted by the Council, a plan was accordingly worked out for the establishment of four such laboratories, namely, the Central Laboratories at Karachi, and three Regional Laboratories at Dacca, Lahore and Peshawar, to take care of industrial problems specific to these areas. These laboratories comprise 21 functional research divisions, allocated among them according to the requirements of the various regions. While the planning and construction of these laboratories are still proceeding, arrangements were made early for setting up the nuclei of the laboratories in temporary buildings.

This was considered a matter of importance, because it is only work done and results achieved that can lend meaning and reality to organisational activities and, moreover, the progress of the nucleus phase directed towards the solution of urgent industrial problems of the country would ensure a sound, organic growth of the research organisation and its laboratories. As an indication of the rapid pace at which the activities of the Council have progressed, it may be stated that, starting with a complement of only four research workers in 1953, the staff of the Central Laboratories, which are housed in temporary buildings covering about 50,000 sq. ft. of floor area, has grown to over 280 members including scientific personnel of various cadres and other technical and accessory services. The progress of the three Regional Laboratories which started about two years later is following the same steeply ascending curve.

One of the aims of the Council relates to the collection and dissemination of scientific and industrial information. To cope adequately with this sector of its activities, a scientific and technical documentation centre (PANSDOC) has been recently set up under the Council with the assistance of UNESCO and the association of three UNESCO expert advisers. With the phenomenal increase in the volume of scientific research, keeping pace with scientific literature even in a narrow, specialised field has become a major problem in the advancement of scientific knowledge, and a virtual despair of individual research workers. The establishment of PANSDOC will, it is hoped, considerably relieve the situation by supplying the needed publications to institutions and individual workers in the form of microfilms and photocopies, and also translations of research papers from other languages into English.

Alongside of these activities and the rapid progress made with them, the need for bringing out a Journal of Scientific and Industrial Research under the Council has been increasingly felt. At the same time, however, it was realised that it would be wiser to defer such an undertaking till research contributions from the various laboratories of the Council and through research schemes financed by it at the Universities and other research institutions of the country had become available in sufficient volume to run the journal successfully without adversely affecting the publication of the existing scientific journals of the country. Happily, as a result of research work carried out under the Council during the last four years over a wide range of problems relating to the development of the natural resources of the country, a considerable volume of publishable material has accumulated, and it was felt that the publication of the journal could not brook any further delay. It will be initially published as a quarterly, but every effort will be made to develop it into a monthly journal as early as possible. Such as it is, we are fully conscious of the shortcomings of this first issue of the journal. It is none the less hoped that it will be fulfilling an urgent need for the dissemination of scientific and technological information on the one hand, and liaison with industry on the other. The extent to which it may be able to fulfil these dual functions, and further serve as an effective medium for the publication of results of original researches in both pure and applied fields, will be the true measure of its success.

S. S.

STUDIES IN THE ALKALOIDS OF RAUWOLFIA SERPENTINA, BENTH. AND THE MODE OF THEIR OCCURRENCE

Isolation of a new Hypotensive Factor and other Alkaloidal Complexes from the Roots

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IN the last communication on the alkaloids of Rauwolfia Serpentina, Benth.,[1] the importance of handling fresh drug material was stressed, as carelessly collected and stocked samples of roots gave very low yields of crystalline bases. Around the same time, it was noted by the author that while dialysis* of fresh uncrushed sprouts from the germinated Bengal gram (Cicer Arietenum, Linn.) with alcohol gave three crystalline products,[2] two of which later proved to be free isoflavones[3] the third being identified as asparagine,[4] none of these constituents could be isolated from air-dried sprouts, due apparently to enzymic and oxidative degradation.

Profiting from these observations on a resumption of studies in the alkaloidal constituents of Rauwolfia serpentina after a long unavoidable break during the war and its aftermath, fresh undried roots harvested from an experimental plantation in East Pakistan were chopped into 2 to 3 centimeter lengths and dialysed five times with alcohol. The dialysate which accounted for about 80% of the assayed alkaloidal content of the roots yielded on removal of the solvent 5% of semi-solid matter on air-dried basis, as against 10 to 12% extractive from the alcoholic percolates of the dried powdered roots, the non-alkaloidal ballast, which greatly complicates isolation work, being thus reduced by about half in this process. The product thus obtained has been resolved into four alkaloidal factors, noted below along with their paper chromatographic evaluation. In view of their probable therapeutic importance as a whole, the first three of these factors have been provisionally assigned names in accord with the nomenclature of the ajmaline series of bases, for the convenience of future reference.

1. Petroleum ether soluble 'oleo-alkaloid' fraction—resajmaline—greenish, viscous oily liquid containing the fatty matter, serposterol, and unsaturated higher alcohols along with around 2.3% reserpine[5] and 0.5% rescinnamine,[6] along with some other weaker bases and only traces of ajmaline. It is soluble in ethyl acetate, ether and petroleum ether, fairly so in alcohol and methanol.

2. Ethyl acetate-benzene soluble akaloidal complex—ajmalexine—forming a cream coloured powder with a concentration of the weaker Rauwolfia bases including 5.5% of reserpine, 2.5% of rescinnamine and some hitherto unknown substances with green and yellowish orange fluorescence. It is soluble in ethyl acetate, mostly soluble in benzene, fairly so in alcohol and methanol, and insoluble in petroleum ether.

3. Serpajmaline fraction, light cream coloured powder soluble in water and also in some partially miscible solvents, mainly containing the stronger bases serpentine, serpentinine, ajmaline and two unknown substances.

4. A cream coloured powder, soluble in water as well as in a mixture of alcohol and non-miscible solvents, containing the stronger bases and two unknown substances with a greenish and a yellowish orange fluorescence.

A reddish, syrupy, water soluble fraction forming the non-alkaloidal ballast was eliminated in the process of separation, which is based on the varying solubilities of the fractions in water and various polar and non-polar organic solvents, without the use of any chemical reagents. Two minor quantities of intermediate alkaloidal fractions were also separated off in the process which will be dealt with later.

While exhaustive studies in the therapeutically significant constituents of these factors and the mode of their occurrence are in progress, it may on the basis of the present pharmacological studies be reported that fraction No. 3 (serpaj-

* The expression 'dialysis' is considered appropriate as the unruptured cell membrances serve as a dialysing medium.

maline), which is chromatographically free from reserpine and other weaker bases and accounts for about 40% of the total alkaloids, is much more potent in its hypotensive activity than pure reserpine, without the complicating feature of the latter's sedative and central depressant action.

From the description of the various factors isolated from the alcoholic dialysate of the uncrushed roots, it will be further seen that none of them correspond to what could be termed as an 'oleo resin', an expression introduced by some of the later workers in this field, and that reserpine and rescinnamine are concentrated in the lipoid soluble factors, ajmalexine and resajmaline, the latter of which consists of fatty matter, serposterol, and higher alcohols[1] with an alkaloidal complex which in contrast to the free bases is readily soluble in petroleum ether. It will also be observed that rescinnamine and reserpine are present in fraction No. 2 (ajmalexine) in a ratio of 2:5 and even in the petroleum ether soluble fraction, which is neglected in the Ciba process for the isolation of reserpine,[7] the two bases occur in a ratio of 1:5, whereas rescinnamine seems to have been isolated in only very minute quantities from the Rauwolfia roots.

With reference to the isolation of reserpine, it may be recalled that in the last communication of the present author,[1] it was reported that the 'neutral fraction' of the alcoholic extracts of the whole roots and the bark gave a white crystalline alkaloid melting at 234°C., which appeared to have an amphoteric character. At that stage no name was assigned to this weak base on account of its doubtful uniformity, but working subsequently with larger quantities of the base and its mother liquors it was possible early in 1940 to obtain from them an alkaloid with a melting point varying with the rate of heating between 262-264°C. and 270-272°C., as against the melting points 262-263°C. and 272°C., later reported for reserpine. Recently, a product melting at 238-240°C. was isolated from the corresponding neutral fraction obtained from the alcoholic extracts of commercially available Rauwolfia roots, which on alternate repeated fractional crystallisation from methanol and acetone yielded two bases which could be identified with reserpine and ajmalicine.

It will be observed that the findings recorded in this communication are in sharp contrast to the results of extensive investigations reported in recent years on the therapeutic activity of various alkaloids and alkaloidal factors obtained from the extracts of dried powdered roots and root bark.[8] Definite conclusion in this regard will have to await further studies which are under way, but already at the present stage of work it would appear that many of the references in respect of the nature of the alkaloidal constituents of the drug and their therapeutic activity, particularly the claim for reserpine as the major therapeutic agent, may eventually have to be drastically revised. The procedure adopted in the present work for the isolation of therapeutically active constituents in their naturally occurring complex form would, moreover, seem to offer a new approach to studies in medicinal plant materials.

Experimental

Isolation of Serpajmaline

16 kg. of fresh undried roots of Rauwolfia serpentina, Benth., corresponding in air-dry weight to 7.650 kg., were chopped into 2 to 3 cm. lengths and soaked with ethanol in a percolator for 48 hours after which the first percolate was drained out. After 5 similar operations a sample of the percolated roots assayed for only 0.3% alkaloids as against 1.3% in the original roots on air-dry weight basis in each case. The combined percolates were completely freed of the solvent in vacuo below 60°C. The resulting semi-solid residue (400 g.) was partitioned between one litre of water and 500 cc. of ethyl acetate whereby the whole of it was divided up between these two phases without leaving any insoluble matter. The lower aqueous layer was repeatedly extracted with ethyl acetate (4.5 litres) till the ethyl acetate layer was found to extract only a negligible quantity of the material and had a slightly yellowish colour. The aqueous layer was then repeatedly extracted with amyl alcohol (6 litres) till further extractions were noted to yield only negligible quantities of residue on removal of the solvent from an aliquot fraction. The combined amyl alcoholic extract was then shaken out repeatedly with water (3 litres). The aqueous extracts on removal of the solvent in vacuo below 60°C. yielded a spongy residue which could be resolved into a light cream coloured powder (95 g.). The amyl alcoholic solution left after exhaustion with water was freed of the solvent and the residue was subjected to the operations carried out on the semi-solid residue left on removal of the solvent from the alcoholic percolates, whereby a second lot of serpajmaline was obtained (20 g.) making for a total yield of 115 g. (1.5%).

Serpajmaline thus obtained softened at 85°C., stuck to the sides at about 100°C. and frothed up at 130°C. Its 1% aqueous solution had a pH value around 6.

Separation of Resajmaline and Ajmalexine

The combined ethyl acetate extracts were freed of the solvent in vacuo and digested with petroleum ether till the petroleum ether did not extract any further quantity of the resulting light cream coloured powder. The petroleum ether extracts gave, on removal of the solvent, resajmaline in a yield of 53 g. (0.7%) , while the light cream coloured powder, ajmalexine, formed 31 g. (0.4%).

Acknowledgement

The author gratefully acknowledges the debt he owes to Dr. Hedayatullah for the invaluable supply of 20 pounds of fresh roots used in this work ; to Dr. Deininger for the pharmacological study of the alkaloidal factors ; to the UNESCO authorities for his secondment to the Central Laboratories ; and to Dr. F. Kaiser of Boehringer, Mannheim, for the paper chromatographic analyses of the alkaloidal factors.

References

1. S. Siddiqui, J. Indian Chem. Soc., **16,** 421 (1939).
2. S. Siddiqui, J. Sci. and Ind. Research (India), **4,** 68 (1945).
3. S. Siddiqui and J.L. Bose, J. Sci. and Ind. Research (India), **4,** 231 (1945).
4. M. Damodaran and C. Singh, Proc. Indian Acad. Sci., **33B,** 159 (1951).
5. J.M. Muller, E. Schlittler and H. J. Bein, Experentia, **8,** 338 (1952).
6. M.W. Klohs, M.D. Draper and F. Keller, J. Am. Chem. Soc., **76,** 2843 (1954).
7. Ciba Ltd., Pakistan Patent 105288 (July 28, 1953).
8. R.F. Woodson, H.W. Youngken, E. Schlittler and S.A. Schneider, *Rauwolfia (Botany, Pharmacognosy, Chemistry and Pharmacology)*, Little, Brown and Company, Boston.

PHARMACOLOGICAL INVESTIGATION OF AN ALKALOIDAL FACTOR OF RAUWOLFIA SERPENTINA

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Comparative studies in the different alkaloidal factors obtained by S. Siddiqui from fresh undried roots of Rauwolfia serpentina and referred to the author for pharmacological investigation, have indicated that one of them, named as "serpajmaline", possesses properties of outstanding clinical value. It is much more effective than reserpine in reducing blood pressure and has no sedative effect.

Methods

Measurements of blood pressure were made on dogs in phenobarbitone narcosis. The *A. Fermoralis* was connected to a mercury manometer. Application — intravenous.

The sedative effect was investigated in mice, using the smoked-plate-method due to *Forst.*[1] Observation time — 4 hours.

Results

The blood-pressure tests showed that serpajmaline has a reducing effect on blood-pressure even when the amount is as low as 0.25 mg./kg. An increase of this amount gives rise to a corresponding intensification of the blood-pressure-reducing action. In the corresponding tests made with reserpine, a content as high as 2 mg./kg. was ineffective. (Observation time — 1 hr.). At a dosage of 1 mg./kg., serpajmaline had a definitely inhibiting action on the blood-pressure effect after bilateral carotid occlusion. At this dosage, reserpine had no effect.

The smallest amount of reserpine for which a sedative action was observed was 0.5 mg./kg.; for serpajmaline in parallel tests, amounts as large as 5 mg./kg., were ineffective, no sedative effect being observed.

It may be concluded from these results that if serpajmaline is used for clinical purposes, the blood-pressure-reducing effect will be stronger than that of reserpine at the same dosage, while the central secondary effects, such as the sedative effect, which are perceived by the patient as unpleasant, are eliminated.

Reference

1. A.W. Forst, Arch. exp. Path. K. Pharmacol., **189**, 288 (1938).

STUDIES IN THE INFLUENCE OF LONG-CHAIN PHENOLIC ADDITIVES ON THE VISCOSITY OF MINERAL OILS

Part 1—Mixture of Mineral Oil with Bhilawanol and its Derivatives

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IN the course of studies in the industrial applications of Bhilawan and Cashew shell liquids, Siddiqui and co-workers have reported the action of the former as an anti-oxidant,[1] and also the marked depression they both exercise on the viscosities of mineral oils.[2] Insofar as some of the problems in the compounding of lubricants for modern engines relate to (a) prevention of oxidation at higher temperatures and (b) control of viscosity over a wide range of working and storage temperatures, it was considered of interest to study the influence of the principal constituents of these shell liquids (namely Bhilawanol, $1,2,3C_6H_3(OH)_2C_{15}H_{27}$, and Anacardol, $C_6H_4(OH)C_{15}H_{27}$) as well as of their derivatives on the viscosity of mineral oils.

Because of the remarkable stability conferred upon suspensions of carbon black in mineral oil by the addition of a small percentage of Bhilawan and Cashew shell liquids, Mathur et al.[2] had investigated the viscous behaviour of mixtures of Bhilawan shell liquid and of Cashew shell liquid with mineral and vegetable oils.[2] They found that in such mixtures the viscosity was not a linear function of the concentration of the shell liquid, but exhibited very definite maxima and minima. These effects were tentatively attributed to the interaction between the polar OH groups of the constituents of the mixtures. Their curves for mixtures of Bhilawan shell liquid with mineral oils of nearly the same viscosity are shown in Figure 1, an especially remarkable feature of which is the steep drop in the curves for the first few per cent of added Bhilawan shell liquid.

Since this phenomenon of viscosity depression can be expected to throw light on the structure of the molecules in the liquid state, it was considered of interest to continue this work with pure liquids rather than indefinite mixtures of products constituting the shell liquids. The present paper deals with results obtained with pure Bhilawanol (which is a catechol derivative with a $C_{15}H_{27}$ side chain in position 3, having an aggregate of two double bonds) and its mono-methyl ether.

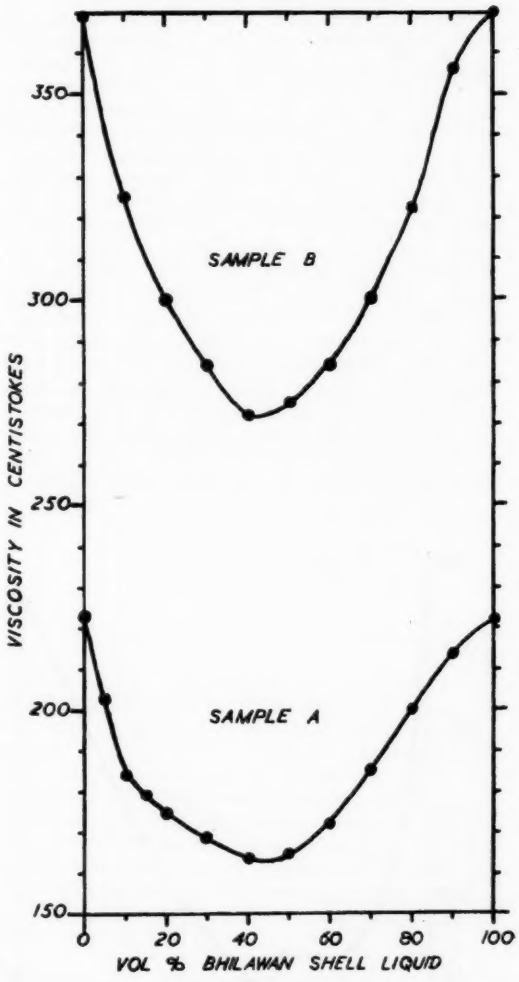

Fig. 1

Experimental

The viscosity of Bhilawanol prepared by the method recorded by Pillay and Siddiqui[3] and distilling at 230° to 235°C./3 mm. of Hg was

found to be about 81 centistokes at 40°C. Bhilawanol was mixed in varying proportions with a 'straight' mineral oil blend having a viscosity of 81.1 centistokes at 40°C. The mixtures were prepared by weighing out the appropriate quantities of the constituents in a tall covered weighing bottle and then shaking well to ensure thorough mixing.

After allowing time for any air bubbles to clear, the kinematic viscosity was measured in a U-tube viscometer No. 2 (British standard specifications) supported vertically in a water-bath, whose temperature was maintained at 40.0° C. ± 0.05° C. (The viscometer had previously been calibrated with sugar solution as recommended in the specifications.) Several readings were taken for each viscosity measurement, the estimated standard deviation of the experimental values being about 0.15 centistoke *i.e.*, about 0.2%. No correction for kinetic energy of flow was made because the times of flow were of the order of 20 minutes, for which this correction produces a change of less than 0.01 centistoke in the measured viscosity. Measurements of the viscosity were made for mixtures with Bhilawanol concentrations differing in steps of about 10%, except for the initial steep part of the curve (for small percentages of Bhilawanol), where it was found necessary to space the readings closer together.

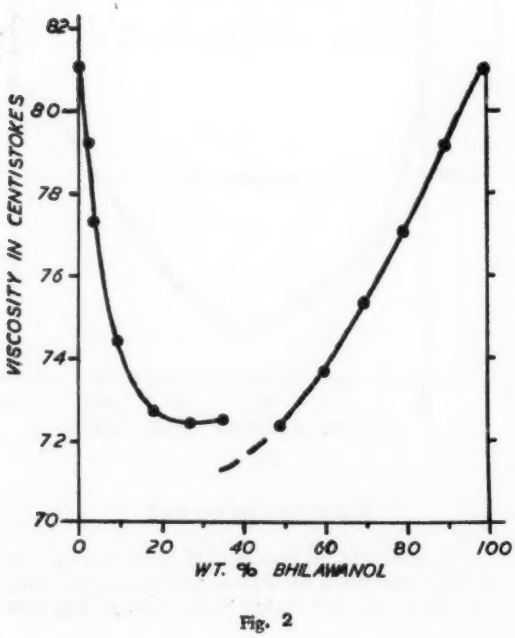

Fig. 2

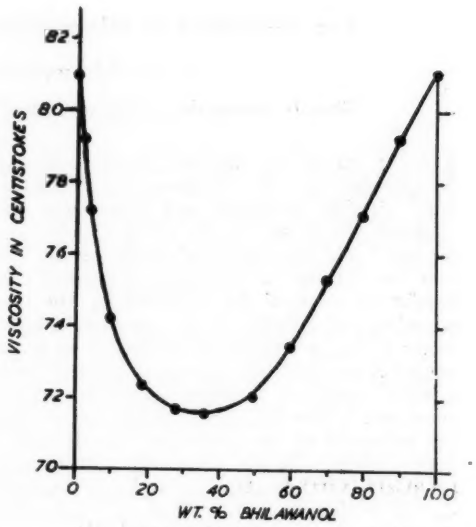

Fig. 3

Readings were taken with *decreasing* Bhilawanol concentrations from 100% to 50% and then with *increasing* Bhilawanol concentrations from 0 % upto 50%.

Results with Bhilawanol

The results are shown graphically in fig. (2). It appears as though *two separate* curves can be drawn, one beginning with pure mineral oil and the other with pure Bhilawanol ; the two curves do not meet in the middle of the diagram. Further examination showed that, near the minimum, the left hand half of the curve will lie above the right hand half of the curve, suggesting that there has been a gradual increase in the viscosity of the Bhilawanol in the course of the observations, which were spread over a period of six days. This was confirmed by a redetermination of the viscosity of the Bhilawanol, when a value of 82.89 centistokes was obtained. This corresponds to an increase of 1.8 centistokes in six days, *i.e.*, an average of 0.3 centistokes per day. A chemical basis for such a steady increase in viscosity is to be found in the gradual oxidation of phenolic compounds, usually accompanied by a deep coloration. The phenomenon is interesting in itself and is being studied separately. The simplest way to reduce observations for comparison with the initial state of the Bhilawanol is to apply to each

TABLE 1

Wt. % Bhilawanol (=100 xx)	Measured viscosity in centistokes	Correction (centistokes)	v=corrected viscosity centistokes	Slope $=\Delta v/\Delta x$	
100	81.09	-.00	81.09	+ 19	Extra-
90.03	79.23	-.02	79.21		polates
				+ 21	to 19±1
79.99	77.13	-.03	77.10		
				+ 18	
69.90	75.36	-.10	75.26		
59.93	73.73	-.29	73.44	+ 18	
				+ 13	
49.15	72.40	-.39	72.01		
				+ 3	
35.93	72.57	-.92	71.65		
27.74	72.49	-.75	71.74		
				- 6	
18.72	72.73	-.36	72.37		
				- 21	
9.63	74.45	-.20	74.25		
				- 46	Extra-
3.89	77.33	-.08	77.25		polates
				-104	to 110±
2.01	79.25	-.04	79.21		15.
				- 94	
0	81.10	-.00	81.10		

reading a correction proportional to the Bhilawanol concentration and to 0.3×(no. of days elapsed since the commencement of the experiment). The uncorrected and corrected readings are both tabulated in table (1), while the corrected results are shown graphically in fig. (3), which affords a perfectly smooth continuous curve.

The very sharp drop in viscosity resulting from a small addition of Bhilawanol to the mineral oil is clearly brought out by the left hand portion of the curve. To ascertain whether the initial part of the curve is linear or otherwise, values of the slope($=\Delta v/\Delta x$) have been calculated in column five of the table, and it is easily seen that these values do extrapolate to a finite value (-110 ± 15) at extremely small concentrations of Bhilawanol. This shows that the initial part of the viscosity graph is linear, *i.e.*, the viscosity depression is approximately proportional to the percentage of Bhilawanol added. The minimum viscosity of the series of mixtures occurs at about 35% by weight of Bhilawanol, which is to be compared with the corresponding recorded value of 40% for Bhilawan shell liquid, cf. Fig. 1. A detailed comparison of the curves of figures 1 and 3 shows that, apart from a shortening of the viscosity scale by a factor of about four, the effect in the pure Bhilawanol is on the whole very much the same as in the composite Bhilawan shell liquid.

Results with Monomethoxy Bhilawanol

It has been suggested by Mathur et al.[2] on the basis of their experiments that the viscosity depression observed in figure (1) is to be attributed to the influence of the polar OH groups of Bhilawanol and their interaction with the molecules of the mineral oil. In

TABLE 2

Wt. % monomethoxy Bhilawanol = 100x	v = Measured viscosity (centistokes)	Slope = $\Delta v/\Delta x$
100.0	16.20	
70.0	14.9	
40.3	14.30	
23.3	14.59	− 5.1
9.10	15.32	− 8.3
5.00	15.66	−11.8
0.00	16.25	

order to examine this suggestion further, experiments were tried with the monomethyl derivative of Bhilawanol, C_6H_3 (OCH_3) (OH) $C_{15}H_{27}$, prepared according to a procedure which will be described elsewhere. This product does not show any changes of colour, etc. due to oxidation, even on standing for many months. The kinematic viscosity of mono-methoxy Bhilawanol, measured at 40°C., is 16.2 centistokes, *i.e.*, about one fifth of the viscosity of Bhilawanol. This confirms that the high viscosity of Bhilawanol is largely due to the interaction of the polar OH groups ; the ratio of the viscosities of the two liquids, *viz.* 1:5, is also consistent with this, cf. the fact that cashew shell liquid with one hydroxyl on the aromatic nucleus has a viscosity about one-third that of Bhilawan shell liquid with two hydroxyls on the nucleus.

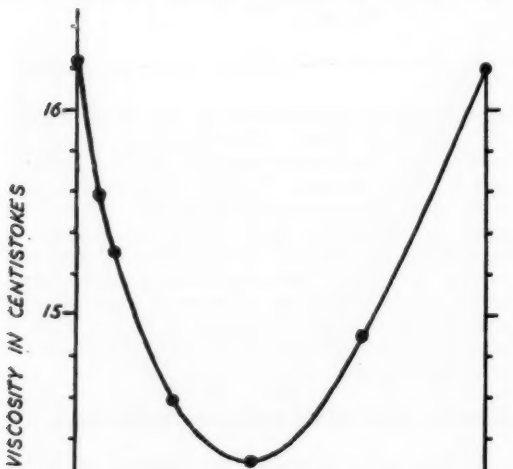

Fig. 4

Monomethoxy Bhilawanol was mixed in various proportions with a straight mineral oil of about the same viscosity, and the kinematic viscosity of the mixtures was measured at 40°C. following the same procedure as with Bhilawanol. (Viscometer No. 2 was still good enough, but the flow times were now of the order of four minutes, thus necessitating a small kinetic-energy correction, amounting to about 0.01 centistoke, in the measured values of the viscosity). The accuracy attained was again of the order of 0.2%. The results are tabulated in table (2), and are shown graphically in fig (4). Due to the small quantity of the monomethoxy Bhilawanol available, the observations could not be spaced very closely ; however, it is seen from fig. (4) that the portion of the curve corresponding to the lower concentrations of monomethyl Bhilawanol can be graphed accurately upto and beyond the minimum in the viscosity curve.

Contrary to expectation, a very marked minimum is present in the viscosity-composition curve. In other ways, too, this curve is very similar to those of fig. (1)and fig. (3)

TABLE 3

Substance	Kinematic viscosity	$I_1 = -\left(\frac{1}{\nu}\frac{\partial \nu}{\partial x}\right)_{x\to 0}$	$I_2 = \frac{1}{\nu}\frac{\nu_o - \nu_{xm}}{x_m}\left(\frac{\partial T}{\partial x}\right)_{x\to 0}$	
Bhilawan shell liquid (a)	370 c.s.	1.7 /part	0.70 per	23 °C/part. (mean)
Bhilawan shell liquid (b)	222 c.s.	1.9 /part	0.66 part	
Bhilawanol	80.1 c.s.	1.35/part	0.36/part	25 °C/part
Monomethoxy Bhilawanol	16.2 c.s.	0.86/part	0.28/part	27 °C/part

(for bhilawan-shell liquid and Bhilawanol respectively), the main difference being a further shortening of the viscosity scale.

Discussion

Since the viscosity depression is present in all the three cases, it becomes necessary to make a quantitative comparison. For this purpose, two "indices" of the viscosity-depression may be defined as

$$I_1 = -\left(\frac{1}{\nu}\frac{\partial \nu}{\partial x}\right)_{x\to 0}, \text{ and } I_2 = \left(\frac{1}{\nu}\frac{\nu_0 - \nu_{xm}}{x_m}\right)$$

where x are the parts by wt. of the three respective products per part of mixture, and x_m is the value of x for the minimum viscosity. I_1 gives a measure of the fractional depression produced per part of the additive for small concentrations of it, while I_2 measures the corresponding quantity for maximum depression. It is readily shown that, if the curve is parabolic to a first approximation, then I_2 will be one-half of I_1. Table (3) shows the calculated values of these indices for Bhilawan shell liquid, Bhilawanol, and monomethoxy Bhilawanol.

It is remarkable that on the whole the two indices of depression show a gradual decrease with the decreasing viscosity of the substance investigated but *not* a sudden drop to a very small value on methylation. The total change in each index is covered by a factor of two. This comparatively small change suggests that the minimum in the viscosity-composition curves is perhaps a secondary phenomenon not *directly* associated with the presence of the active hydroxyl groups. Further indication in this direction is obtained when we calculate the rise in temperature of the mixtures that will produce an equivalent drop in viscosity : this can be calculated as

$$\left(\frac{\partial T}{\partial x}\right)_{x\to 0} = \left(\frac{\partial \nu}{\partial x}\right)_{x\to 0} \Big/ \frac{\partial \upsilon}{\partial T} = \left(\frac{1}{\nu}\frac{\partial \nu}{\partial x}\right)_{x\to 0} \Big/ \left(\frac{1}{\nu}\frac{\partial \nu}{\partial T}\right)$$

It is seen from the last column of table (3) that a value close to 25 °C./part is obtained in each case, the figure for the mono-methoxy Bhilawanol being in fact the highest of the three. The phenomenon of the viscosity depression thus appears to be rather more complex than was suggested by the earlier workers. It is expected that further elucidation of this phenomenon will be provided by studies that are being undertaken with simpler phenolic compounds.

Acknowledgement

Grateful acknowledgement is made to Dr. S. Siddiqui for suggesting the problem, to Mr. Salim Malik for helping in much of the experimental work, and to Mr. Rafiq Ahmad Siddiqui for preparing the Bhilawanol and its monomethoxy derivative.

References

1. S. Siddiqui, A. V. Subbaratanum and V. Sharma, (1946) Indian Patent No. 35567.
2. H. H. Mathur, J. S. Aggarwal and S. Siddiqui, J. Sci. and Ind. Research (India), **9B**, 121 (1950).
3. P.P. Pillay and S. Siddiqui, J. Indian Chem. Soc., **8**, 517 (1931).

INFRARED STUDIES ON SOME FEATURES OF METHYLENE-INTERRUPTED DOUBLE BOND IN AUTOXIDATION OF FATTY ACID ESTERS

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IN continuation of the previous studies[11] it is necessary to describe some specific features of the procedures for the isolation of methyl linoleate, and linolenate hydroperoxides. The investigation on autoxidation with and without agitation have been extended to methyl linoleate and linolenate. Infrared studies on the fatty acid esters and their hydroperoxides have revealed many clues to the mechanism of autoxidation reactions. On the basis of these data and the other experimental facts, the mechanism of the initial attack by oxygen molecule on methylene-interrupted double bonds (5-C system of methyl linoleate and linolenate) has been presented. Some light has been thrown on the catalysis of autoxidation by lipoxidase which is specific in autoxidizing only methylene-interrupted double bonds.

Methyl linoleate and linolenate were freshly prepared by bromination and debromination procedures. All samples were kept under nitrogen and vacuum below -50°C. Autoxidation of methyl linoleate and linolenate (50 g. each) to 10% peroxide contents, was carried out at -10°, 0°, and 24-26°C. in 500 ml. Erlenmeyer flasks without agitation. The same substances were autoxidized at -10°C. under constant agitation by oxygen as previously described.[11] The counter-current extraction between two immiscible solvents was found effective in concentrating the oxygenated products. Unfortunately, the standard procedures for the counter-current extraction[7] distribute the peroxides over several fractions, and under no conditions is the recovery quantitative. Hence, a scheme of manual counter-current extraction, (Fig. 1) was improvized to separate the oxidized from the unoxidized fraction quantitatively. Two immiscible solvents were first obtained by mixing absolute alcohol (distilled over KOH and zinc dust), light petroleum (30°-60°C., and free from unsaturates[14]), and water in the proportions 5:6:1. The resulting petroleum ether and alcohol phases were allowed to separate and used as stock solvents. Both the phases were then cooled to 0°C. In Fig. 1, the S-rows are twelve separatory funnels, each containing 200 ml. of the cold petroleum ether phase. The partially oxidized fatty acid ester was dissolved in the 200 ml. of petroleum ether in S_1. Twelve extractions, each with a 100 ml. portion (A) of the cold alcohol phase, removed all peroxides from S_1. The subsequent extractions, carried out successively in

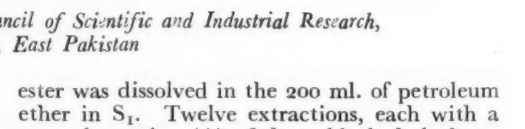

Fig. 1. A Scheme for the Manual Counter-current Extraction.

S_2 through S_{12} by each of these alcohol portions (12A's, Fig. 1), recovered the majority of peroxides and distributed all unoxidized fatty acid ester together with some peroxides in the petroleum ether phase. These remaining peroxides, in S_2 to S_{12} inclusive, were extracted by the number of alcohol portions (2A's—1A—) indicated at the end of the vertical lines extending from the corresponding petroleum ether phase. This additional extraction of peroxides by fresh solvent is not feasible with the standard counter-current procedures.[7] Determination of peroxide values at different steps indicated the efficiency of separation. The peroxide-containing phase of alcohol was kept cooled below 0°C. The pre-cooled oxygen-free nitrogen was bubbled through the above alcohol phase as an added protection. The alcohol phase yielded in general 99.0-99.9% of the oxygenated products formed during the autoxidation of fatty acid esters. The unoxidized fraction obtained from the petroleum ether phase contained only 0.0-0.7% of oxygenated products. All precautions were taken to recover the oxygenated products entirely from the unoxidized fatty acid esters, so that the oxygenated products may represent the initial autoxidation process involved. For the convenience of analysis, an aliquot portion of the oxygenated products was reduced in a

1% alcohol solution by stannous chloride (5 moles/mole of peroxide), agitating with oxygen-free nitrogen.

Methyl linoleate autoxidized at 0° without agitation gave a peroxide concentrate representing 99.9% of the oxygenated products formed during the autoxidation reactions. The corresponding unoxidized fraction isolated was found to be pure methyl linoleate by the following analysis : hydrogen absorption, 1.98 mole/mole ; hydroxyl, 0.0 ; acid value, 0.0 ; carbonyl value, 0.0 ; and polymer, 0.0 ; elementary analysis, C, 77.47 and H, 11.52; calculated from methyl linoleate, C, 77.55 and H, 11.56. The polymer contents were measured by the special micro-technique in distillation.[16] The peroxide concentrate having the peroxide value of 6115 m.e./kg. (theory for methyl linoleate monohydroperoxide, 6125 milliequivalents per kilogram), added 2.92 moles H_2 to yield monohydroxystearic acids (m.p., 75.0-77.5°C;[3] hydroxyl, 1.04 moles/mole). The preliminary polarographic studies indicated that peroxide concentrate consists of 100.5% of hydroperoxide. The reduced peroxide concentrate gave the following analysis : hydrogen absorption, 1.99 mole per mole ; hydroxyl, 1.02 mole/mole ; acid value 0.0 ; carbonyl value, 0.0;[19] and polymer, 0.0 ; elementary analysis, C, 73.41, and H, 10.89 ; calculated for monohydroxy methyl linoleate C, 73.51, and H, 10.97. The infrared analysis of the above samples also indicated production of almost 100% *cis, trans*-conjugated isomer. Two other samples of peroxide concentrates obtained from methyl linoleate autoxidized under identical conditions gave peroxide values of 6100 and 6135 m.e./kg. respectively. It is, therefore, apparent that methyl linoleate forms monomeric monohydroperoxide with the conjugation of double bonds. Similar results were obtained with the autoxidation of methyl linolenate at -10°C. giving only *cis, trans*-conjugated hydroperoxides under otherwise identical conditions. Both methyl linoleate and linolenate involve only 5-C system during the autoxidation reactions in yielding hydroperoxides without any decomposition. The additional double bond in the latter enhances the reaction rate, emphasizing the role of π electrons (cf. arachidonate linolenate linoleate).

Under somewhat more drastic conditions, the hydroperoxides were found to decompose without initiating any polymer formation. The peroxide concentrates (99.0-99.7%) from methyl linoleate autoxidized below 0° under agitation (including one particular case in which 20% of the fatty acid ester was oxidized) gave peroxide values in the range, 5500-5650 m.e./kg. and the reduced peroxide concentrates showed polymer contents, 0.0. Methyl linolenate when oxidized at 0° without agitation yielded peroxide concentrates of 5690 m.e./kg. without any polymer formation. It may be possible that the peroxide decompositions under these conditions do not initiate active free radicals to give rise to polymers in conformity with the information available.[12]

In another series of experiments, the drastic conditions were used with the inevitable results of polymer formation. The peroxide concentrates from methyl linoleate and methyl linolenate, autoxidized at 24-26° without any agitation indicated peroxide values, 5400 m.e./kg. and 3450 m.e./kg. ; their reduced states had polymer contents, 16%, and 31% respectively. The agitation caused 20-25 times faster oxidation, accompanied by greater decomposition of peroxides and polymer formation. Bateman[2] and Bolland[4] with their co-workers have employed the conditions in these last series of experiments and consequently may not have taken into consideration the initial reactions of autoxidation that yield hydroperoxides quantitatively.

After establishing the proper conditions for study of the initial autoxidation processes, it is justifiable to obtain information on the structures of relevant fatty acid esters and oxygen and on their reactivity towards oxidation. With this end in view, the following attempts were made in order to throw some light on the mechanism of autoxidation.

The susceptibility of fatty acid esters to autoxidation, increasing with the number of methylene-interrupted *cis*-double bonds may be inferred from the infrared studies (LiF spectra) at the region of 3.30μ (Fig. 2.) on the isomers and derivatives of methyl linoleate. The amounts of absorption at this region for the different substances are : lino-elaidate (*trans, trans*-non-conjugated), nil (curve 1) ; conjugated isomers, equivalent to that of methyl oleate (curve 2) ; conjugated linoleate hydroperoxides (curve 3), conjugated isomer ; and methyl *cis, cis*-linoleate (curve 4), twice that of oleate. Following the observation of Adams and Auxier[1] in other fatty acids, the infrared absorption at 3.30μ for the linoleate isomers indicates consistently the reactivity of alpha methylenic hydrogen atoms and consequently arises due to $-CH_2-$. The stereochemical configurations play a great role in such reactivity. Herman and Reeves in their recent book on theoretical organic chemistry[9] have, on

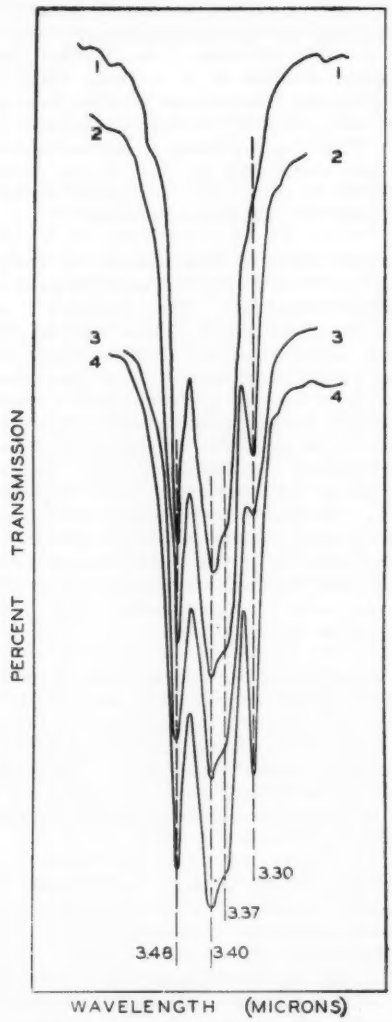

Fig. 2. Infrared Absorption Spectra. Active Methylene groups in the isomers and derivatives of Methyl Linoleate.

quantum mechanical basis, emphasized the non-localization of double bond and spread of electrons over 4-C in conjugated diene as in conjugated linoleate, affecting the alpha methylenic group just as a double bond. Similarly, the spread of π electrons over 5-C in the non-conjugated linoleate with an increased influence on alpha methylenic group is envisaged. The preliminary experiments with the linoleate isomers indicate the different rate of hydroperoxidation according to the alpha methylenic activity. The conjugated linoleate is already known to react with oxygen by ionic 1:4 addition (electrovalent bond) to form 6-membered ring peroxide and so is rubrene and anthracene by apparent covalent bonds. In between these extremes there should be many transition bonds, as it is known today about the cobalt complexes with oxygen molecule[5] and iron porphyrin complexes (oxyhemoglobin and methhemoglobin in particular).

On the other hand, O_2 contains an even number of electrons. However, the ground state of O_2 contains two unpaired electrons, which make O_2 paramagnetic. Though the oxygen molecule is very inactive, it can be attached as a ligand either in such a way that after pairing of those two electrons, a pair of electrons may be used in filling up the needs of substances to be oxidized, thus forming a 'dative bond' (cf. oxyhemoglobin), or in a binuclear complex with an oxygen bridge, each one of the unpaired electrons of O_2 may form a pair with those available from other reactants (anthracene, terpene, and rubrene and the conjugated dienes).

From the foregoing information, it seems probable that oxygen may act as a ligand to the five-carbon system of fatty acid esters through a number of transition complexes to overcome the energy barrier. These concepts in conjunction with the mechanism of oxygen-olefin interaction, previously reported,[12] the attack on 5-C system by oxygen molecule may be graphically represented as in Fig. 3. These processes (I-VII, Fig. 3) yield two positional isomers of linoleate conjugated hydroperoxides (9-, and 13-) which have been described as the products of autoxidation [3, 11, 12] The rearrangement of the non-conjugated peroxy radical to the conjugated form as proposed by Bateman[2] becomes open to question by the isolation of non-conjugated hydroperoxides from the photo-chlorophyll-oxidized linoleate[11,12] which probably involved free radicals. [12,20] Harrison and Wheeler[8] also isolated the non-conjugated products from the reactions of linoleate, supposedly involving free radicals. The limitation of the isomerization to one double bond next to the hydroperoxyl group [2,19] may also speak against allylic radical mesomerism. Furthermore, the complex formation may allow formation of *cis-cis*-conjugated products which have been reported by Sephton and Sutton.[18] It is difficult to predict the behaviour of the allylic radical on the surface of the protein moiety with many active centres in lipoxidase which also autoxidizes linoleate to the definitive products.

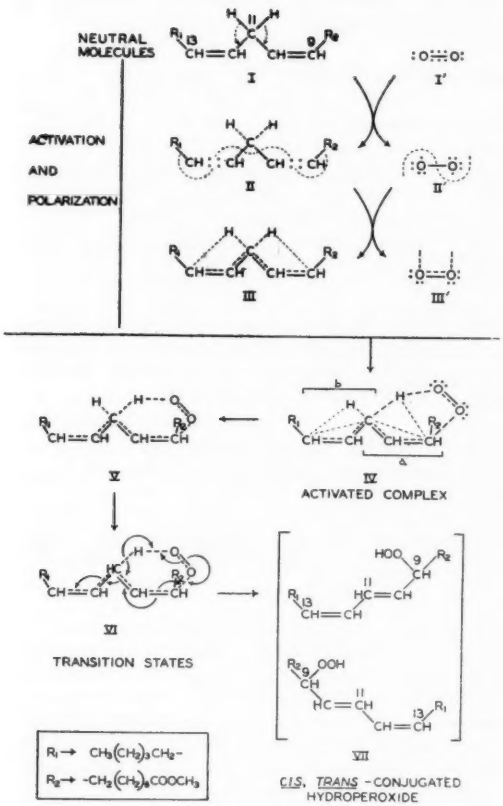

Fig. 3. Initial attack by oxygen molecule on methylene-interrupted double bonds.

However, the polar characteristics provided by the structures (I-IV, Fig. 3) may give rise to a certain specific charge distribution in the 5-C system of each molecule and explain the specificity[10] of lipoxidase-catalyzed autoxidation. Oxygen may act as a prosthetic group[10,15] in the ternary enzyme complex[6] consisting of enzyme, oxygen molecule and fatty substrate. The lipoxidase may, thus, incorporate each molecule of oxygen individually to a molecule of the fatty substance. The optical rotation of the lipoxidase-catalyzed autoxidation products is direct evidence of this organized individual attack on each molecule.

One particular batch of sodium linoleate was autoxidized in the presence of lipoxidase as described in the earlier publications.[13] The peroxide concentrate, isolated quantitatively by counter-current extraction, constituted 99.3% of the oxygenated products formed during the lipoxidase-catalyzed oxidation. On storage at -50°C. as a 1% solution in alcohol, the peroxide concentrate precipitated some gelatinous polymer materials (4.6 per cent of total peroxide concentrate by weight). The peroxides (94.7% of peroxide concentrate) were separated and reduced by stannous chloride. The reduced products were proved by chemical and infrared analyses to be same as the ordinary autoxidation products, except for the optical rotation. The polymer formation may be attributed to minor side reactions in a complicated system.

The mechanism proposed for methylene-interrupted double bonds (five-carbon system) may account for : (a) the energy requirements and the formation of only two positional conjugated isomers ; (b) the effects of different spatial and electronic configurations, and the possible olefin-oxygen interactions involving a ligand and thereby yielding the initial molecules of hydroperoxides ; (c) the independent hydroperoxidation in fatty acid esters below 0° for an indefinite length of time in complete darkness ; (d) the specific catalytic effects of lipoxidase in autoxidizing each individual molecule of fatty acids with the five-carbon systems and maintaining the plane of symmetry, responsible for optical rotation.

Further details will be published later.

References

1. K. Adams and R.W. Auxier, Official Digest, Fed. Paints and Varnish, **322,** 669 (1951).

2. L. Bateman, Quart. Rev., **8,** 147 (1954).

3. S. Bergstrom, Arkiv. Kemi Mineral. Geol. **A21,** 14 (1945); Nature, **156,** 717 (1945).

4. J.L. Bolland and G. Gee, Trans. Farad Soc., **42,** 239, (1946).

5. M. Calvin, R.H. Bailes and W.K. Wilmarth, J. Am. Chem. Soc., **68,** 2254 (1946) ; M. Calvin, and C.H. Barkelew, ibid. **68,** 2267 (1946) ; T. Tsumaki, Bull. Chem. Soc., Jap., **13,** 2522 (1938).

6. B. Chance, J. Biol. Chem. **151,** 553 (1943); Adv. Enzym., **12,** 153 (1951).

7. L.C. Craig and D. Craig, in *Technique of Organic Chemistry*, Vol. III, edit. by

A. Weissberger, p. 259, Interscience Publishers, Inc., New York, 1950.

8. S. Harrison and D.H. Wheeler, J. Am. Chem. Soc., **76,** 2379 (1954).

9. P.H. Hermans, *Introduction to Theoretical Organic Chemistry*, Edited and translated by R.E. Reeves, pp. 71-75, Elsevier Publishing Co., New York, 1954.

10. R.T. Holman and S. Bergstrom, *The Enzymes*, Vol. II, Part I, p. 559, Academic Press Inc., New York, 1951.

11. N.A. Khan, Biochem. et Bioph. Acta, **16,** 159 (1955.)

12. N.A. Khan, Canad. J. Chem. **32,** 1149 (1954).

13. N.A. Khan, Arch. Biochem. and Biophys., **44,** 147 (1953).

14. H.W. Melville and H.R. Cooper, J. Chem. Soc., p. 1988 (1951).

15. L. Michaelis, Progress in Science, **5,** 119 (1947).

16. R.F. Paschke, J.R. Kerns and D.H. Wheeler, J. Am. Oil Chemists' Soc., **31,** 5 (1954).

17. H. Schlenk, in *Progress in the Chemistry of Fats and other Lipids*, Edit. R.T. Holman, W. O. Lundberg and T. Malkin, p. 243, Academic Press, Inc., 1954.

18. H.H. Sephton and D.A. Sutton, paper No. 53, presented at the Fall meeting of the American Oil Chemists' Society, Philadelphia, Pa., 1955.

19. S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., 1949.

20. N. Uri, J. Am. Chem. Soc., **74,** 5808 (1952).

OXIDATION OF SODIUM SULPHIDE WITH NITRIC OXIDE

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SINCE the close of the eighteenth century, several workers have studied the reduction of nitric oxide to nitrous oxide by alkali sulphides [1-8]. However, they did not study the reactions in any great detail. About the year 1929, Dunnicliff and co-workers[9] started a detailed study of the oxidation-reduction systems. In collaboration with Kotwani,[10] Soni and Hamid,[11] respectively, Dunnicliff studied the oxidation of hydrogen sulphide by chromic acid, potassium dichromate, soluble and insoluble chromates etc. Oxidation of sulphuretted hydrogen was the main purpose of these studies.

In 1929, Pierce,[12] published a paper entitled "Interaction between nitric oxide and hydrogen sulphide," in which he established that the gases react together with the formation of water, sulphur and nitrogen:

$$2NO+2H_2S=2H_2O+2S+N_2$$

Two years after the publication of this paper Dunnicliff, Sardar Mohammad and Jai Kishan[13] attempted to study the interaction between nitric oxide and hydrogen sulphide in the presence of water, where they detected ammonium sulphide among the intermediate products. They also began a study of the action of nitric oxide on ammonium sulphide, but do not appear to have followed it through. This subject, therefore, has not so far been investigated in any detail and the information about this reaction is sketchy.

In these laboratories the work has been carried out on oxidation of sodium sulphide and polysulphides against potassium permanganate,[14] and later on against potassium dichromate.[15] These reactions were studied in liquid-liquid phase, whereas the present communication deals with the reaction between the nitric oxide (a gas) and sodium sulphide solution.

This reaction differs in many respects from the "interaction between nitric oxide and hydrogen sulphide," already referred to above, in the fact that whereas H_2S is acidic, sodium sulphide is basic due to hydrolysis in solution :

$$Na_2S+H_2O=NaOH+NaHS$$

The problem of the oxidation of sodium sulphide is of considerable academic and theoretical importance. The present investigation attempts to provide quantitative data about the intermediate and final products formed in the liquid as well as in the gaseous phase.

Preparation of Raw Materials

Nitric oxide was prepared by dripping a concentrated solution of sodium nitrite into an acidified solution of ferrous sulphate :

$$2HNO_2+2FeSO_4+H_2SO_4=2NO+Fe_2(SO_4)_3+2H_2O$$

The gas was contaminated with some traces of NO_2 and was, therefore, purified by passing through a concentrated solution of caustic soda and dried over solid sodium hydroxide to free it from nitrogen peroxide and moisture.

Sodium mono-sulphide crystals were taken and washed with distilled water and finally with absolute alcohol. The crystals were filter-pressed and then dried in a vacuum desiccator for 10-15 minutes. Sodium sulphide solution was titrated against standard iodine solution (a known volume of the solution was run into a known excess of standard iodine solution acidified with acetic acid. The excess of iodine was titrated back against standard thiosulphate solution).

Experimental

(a) Quantitative study of the reaction : The interaction between nitric oxide and sodium sulphide was studied at *room temperature only* (at about 25 °C.) and by taking various concentrations of the sulphide solution.

Hydrogen gas was used to provide an inert atmosphere as nitric oxide reacts with atmospheric oxygen to form nitrogen dioxide.

Dunnicliff and co-workers[15] used carbon dioxide while studying the reaction between hydrogen sulphide and nitric oxide. In the present inventigations, however, carbon dioxide could not be employed as it is absorbed by sodium sulphide solution.

Preliminary experiments showed qualitatively the presence of thiosulphate, sulphate, poly-sulphides, nitrite and ammonium ions in

solution, and sulphur in the precipitate. The colour of sodium sulphide solution underwent various changes, starting from light yellow to deep orange (in the case of strong solution). Finally the solution became quite colourless. At the intermediate stages sulphur decreased in quantity thereby showing the formation of poly-sulphides. At successive stages of change of colour, the solutions were critically examined and analysed so as to trace the course of the reaction.

This gave an approximate idea about the course of reaction. In the initial stages sulphide, thiosulphate, sulphate (traces), nitrite and ammonium along with free sulphur were present, while at the final stage, only sulphate, nitrite, and ammonium were present in the solution and free sulphur in the precipitate, while sulphide and thiosulphate were totally absent. Nitrate was not detectable, even by very delicate tests : tetrathionates were also absent. (Tetra-thionates if formed would be decomposed by the strongly alkaline solution.)

(b) Quantitative analysis of the products of reaction in solution : (1) After the completion of the reaction at each stage, the solution was filtered in order to retain the precipitate of free sulphur, and the filtrate was analysed.

Sulphate—was estimated by precipitating it as barium sulphate in the cold.

Thiosulphate—at the final stage of oxidation thiosulphate was estimated by titration against standard iodine solution. Control experiments showed that if the amount of nitrite in the solution was very small, it did not interfere during the estimation of thiosulphate. Estimation of thiosulphate at the intermediate stages was carried out after removing the sulphide as cadmium sulphide. Thiosulphate was oxidised with bromine to sulphate and estimated along with sulphate remaining behind as barium sulphate. By substracting the amount of sulphate originally present as such, the quantity of thiosulphate was obtained.

Sulphide: Thiosulphate and sulphide were oxidised by bromine and estimated as barium sulphate along with the sulphate originally present. The amount of sulphate due to sulphide was obtained by substracting the sulphate due to thiosulphate and sulphate as such.

Ammonium: The reaction solution after the removal of sulphur (by filteration) was heated with strong sodium hydroxide solution and the ammonia evolved was absorbed in 0.1 N sulphuric acid.

Nitrite: (*a*) *By reduction with Devarda's Alloy.* The solution was warmed with Devarda's alloy until the evolution of hydrogen ceased and then sodium hydroxide solution was added, the ammonia evolved being absorbed in standard sulphuric acid. By substracting the amount of ammonia corresponding to the already estimated ammonium, the quantity of nitrite was determined.

(*b*) Sulphide was removed by $CdCO_3$ and the 'nitrite' was determined by titration against standard $KMnO_4$. Control experiments indicated that thiosulphate in this case did not interfere with the nitrite present.

Free Sulphur: The precipitate of sulphur was washed, dried at 90° and weighed as such.

Results and Discussion

The reaction was studied by passing nitric oxide gas into sodium sulphide solution for various intervals of time and the products were analysed at regular stages. The gaseous products of the reaction were analysed by a modified form of the apparatus used by Milligan[1] and later on by Dunnicliff[17] and S. Mohammad for the same purpose.

It has been found that :

(1) When nitric oxide was passed into sodium mono-sulphide solution of various strengths, sodium poly-sulphides, thiosulphate, sulphate and sulphur along with some ammonium and nitrite ions were formed ;

(2) In the gaseous phase, the products of the reaction were nitrous oxide and nitrogen, when an excess of nitric oxide was used, and nitrogen only when a strong solution of sodium mono-sulphide was employed ; (Tables No. 5 and 6 respectively).

(3) Sodium disulphide and trisulphide were also decomposed by nitric oxide giving thiosulphate, sulphate and sulphur along with ammonium and nitrite ions ;

(4) After the complete oxidation, nearly half the amount of sulphur (calculated on the basis of mono-sulphide) was present as free sulphur, and the remaining half could be accounted for in the sulphate ; (Tables 1 and 2).

(5) When nitric oxide was passed into sodium disulphide solution of various concentrations, formation of some

higher polysulphides took place, indicated by the decrease in the amount of sulphur and a deep orange colour of the solution, (due to polysulphides);

(6) When sodium tri-sulphide was oxidised by nitric oxide, no decrease in the amount of free sulphur was observed, thus eliminating the possibility of the

TABLE 1

TABLE SHOWING THE RELATIVE AMOUNT OF SULPHATE AND FREE SULPHUR PRESENT IN THE SOLUTION AFTER COMPLETE OXIDATION OF $Na_2S.\ 9H_2O$ BY NITRIC OXIDE

$Na_2S\ 9H_2O$ dissolved per 500 ml. = 24.006 g. (M/5)
Nitric oxide was passed into M/5 sodium monosulphide ($Na_2S.\ 9H_2O$) solution for 65-75 hours.
The composition of the solution is expressed in g./500 ml.

Results of three experiments performed

Experiment No.	Free sulphur	Barium sulphate from sulphate	Sulphate formed as SO_4''	Sulphur accounted from SO_4''	Total sulphate determined	Sulphur theoretical	Difference
	g.	g.	g.	g.	g.	g.	g.
1	1.6795	11.981	4.569	1.5245	3.204	3.206	0.002
2	1.6645	11.2185	4.6185	1.5400	3.245	3.206	0.0015
3	1.6675	11.21275	4.608	1.5360	3.2035	3.206	0.0025

TABLE 2

TABLE SHOWING THE RELATIVE AMOUNT OF SULPHATE AND FREE SULPHUR PRESENT IN THE SOLUTION AFTER COMPLETE OXIDATION OF $Na_2S.\ 9H_2O$ BY NITRIC OXIDE

$Na_2S.\ 9H_2O$ dissolved per 500 ml. = (M/10) = 12.003 g.
Nitric oxide was passed into M/10 sodium monosulphide ($Na_2S.\ 9H_2O$) solution for 33.5 hours.
The composition of the solution is expressed in g./500 ml.

Results of three experiments

Experiment No.	Free sulphur	Barium sulphate from sulphate	Sulphate formed as SO_4''	Sulphur accounted from SO_4''	Sulphate sulphur	Sulphur theoretical	Difference
	g.	g.	g.	g.	g.	g.	g.
1	0.8420	5.4315	2.2800	0.7592	1.6012	1.6030	0.0018
2	0.8315	5.5965	2.2995	0.7695	1.6010	1.6030	0.0020
3	0.8365	5.5720	2.2920	0.7640	1.6005	1.6030	0.0025

TABLE 3

TABLE SHOWING RELATIVE AMOUNT OF SULPHUR PRESENT IN VARIOUS COMPOUNDS WHEN NITRIC OXIDE WAS PASSED INTO M/5 SODIUM MONOSULPHIDE ($Na_2S.9H_2O$) SOLUTION FOR VARIOUS INTERVALS OF TIME

Amount dissolved per 500 ml. M/5 = 24.066 g.

Hours for which nitric oxide was passed = 65.75 (about)

500 ml. of the solutiou was taken for the reaction.

The composition of the solution is expressed in gms. /500 ml.

No.	Time in hours	Free sulphur	Sulphate formed as SO_4''	Thio-sulphate formed as S_2O_3''	Sulphur Accounted from			Total sulphur deter-mined	Sulphur theore-tical	Difference
					SO_4''	S_2O_3''	Unde-composed S''			
1.	.79	0.023	Nil	Negligible	Nil	—	3.184	3.204	3.206	0.002
2.	1.833	0.0615	0.0255	0.02097	0.00716	0.012	3.12314	3.2038	3.206	0.0022
3.	3.00	0.1050	0.071	0.13284	0.02366	0.076	2.99834	3.2030	3.206	0.003
4.	6.5	0.1985	0.4967	0.2962	0.1656	0.1695	2.6704	3.2040	3.206	0.002
5.	13.5	0.4652	0.9575	0.41602	0.31916	0.2380	2.18114	3.2035	3.206	0.0025
6.	18.5	0.44272	1.4796	0.52003	0.3932	0.2975	2.0868	3.2047	3.206	0.0013
7.	22.00	0.6685	1.4895	0.76160	0.4965	0.4357	1.6043	3.205	3.206	0.001
8.	33.5	0.9785	2.8474	0.56023	0.89583	0.3205	1.20867	3.203	3.206	0.003
9.	65.75	1.6300	4.7250	Nil	1.5750	Nil	Nil	3.205	3.206	0.001

formation of higher polysulphides (tetra and penta) ;

(7) Sodium nitrite solution remained unaffected by nitric oxide ;

(8) Sodium thiosulphate solution was decomposed by nitric oxide giving sulphate and sulphur. Ammonium and nitrite ions were detected in traces; (Table 7).

(9) When nitric oxide was passed into a mixture of sodium thiosulphate and sodium nitrite solution, the thiosulphate decomposed to give sulphate and sulphur, and a very minute decrease in the amount of 'nitrite' was observed.

The studies on the relative amount of various compounds lead to the conclusion that two different products were formed in the solution:

(1) The primary products of the reaction in solution were thiosulphate, polysulphides and sulphate, and a precipitatie of free sulphur.

(2) The secondary products of the reaction in solution were nitrite and ammonium ions.

The gaseous products of the reaction were N_2O and N_2 when an excess of nitric oxide was used and the solution of sodium sulphide was weak. When strong solution of sodium sulphide was employed, only nitrogen was evolved.

TABLE 4

TABLE SHOWING THE RELATIVE AMOUNT OF SULPHUR CONTAINED AS DIFFERENT COMPOUNDS WHEN NITRIC OXIDE WAS PASSED INTO M/SODIUM MONOSULPHIDE ($Na_2S.9H_2O$) SOLUTION FOR DIFFERENT INTERVALS OF TIME

Amount dissolved/500 ml. = 12.003 g.
Time for which the gas was passed = 33.5 hours.
500 ml. of the solution was taken for the reaction.
The composition of the solution is expressed in g./500 ml.

No.	Time in hours	Free sulphur	Sulphate formed as SO_4''	Thio-sulphate formed as S_2O_3''	Sulphur accounted from			Total sulphur determined	Sulphur Theoretical	Difference
					SO_4''	S_2O_3''	Unde-composed			
1.	3.0	.98	.9369	.10400	.03123	.595	1.40633	1.5950	61.603	.00794
2.	4.5	.216	.1830	.15120	.0610	.0865	1.2385	1.6020	1.603	.001
3.	7.5	.1995	.4968	.33124	.16516	.1895	1.04094	1.5951	1.603	.0079
4.	13.5	.3895	.96375	.39417	.32125	.2255	0.65905	1.5953	1.603	.0077
5.	22.00	.7575	1.370	.34086	.5035	.1950	0.1408	1.5968	1.603	.0062
6.	33.50	.8045	2.3817	Nil	.7939	Nil	Nil	1.5984	1.603	.0046

TABLE 5

ANALYSIS OF THE GASEOUS PRODUCTS OF THE REACTION BETWEEN NITRIC OXIDE AND SODIUM SULPHIDE SOLUTION

Results of three experiments

No.	Volume of the gas. cc.	Volume of hydrogen cc.	Volume after combustion cc.	Contraction cc.	Nitrogen cc.	Composition	
						Nitrous oxide %	Nitrogen %
1.	14.0	26.6	36.0	4.6	9.4	32.85	67.15
2.	14.7	27.1	36.8	5.0	9.7	34.00	67.00
3.	15.0	28.3	37.4	5.9	9.1	37.3	62.70

Sodium sulphide got hydrolyzed and then reacted with the gas, because it was found that N/10 solution (sodium mono-sulphide) was more than 86.4% hydrolyzed in water according to the equation :

$$Na_2S + H_2O = NaHS + NaOH \quad .. \quad (1)$$

The reaction between nitric oxide and sodium sulphide proceeded according to the stages mentioned below.

TABLE 6

ANALAYSIS OF THE GASEOUS PRODUCTS OF REACTION BETWEEN NITRIC OXIDE AND AN EXCESS OF SODIUM SULPHIDE SOLUTION

Results of three experiments

No.	Volume of the gas cc.	Volume of hydrogen cc.	Volume after combustion cc.	Contraction cc.	N_2 cc.	N_2O %	N_2 %
1.	23·3	34·1	57·3	0.1	23.2	0.0	100
2.	25.1	36.6	61.5	0.0	25.1	0.0	100
3.	22.5	35·9	58.4	0.0	22.5	0.0	100

TABLE 7

TABLE SHOWING THE DECOMPOSITION OF N/10 ($Na_2S_2O_3$ $5H_2O$) SODIUM THIOSULPHATE SOLUTION BY NITRIC OXIDE WHEN NITRIC OXIDE WAS PASSED FOR 10 (TEN) HOURS THROUGH 500 ML. OF THE SOLUTION

THE REACTION SOLUTION WAS ANALAYSED AT INTERMEDIATE INTERVALS

The composition of the solution is expressed in g./500 ml.

Time in hours	1	2	4	6.5	10
Thiosulphate taken as ($Na_2S_2O_3$) ..	12.410	12.410	12.410	12.410	12.410
Thiosulphate taken as ($S2O_3''$) ..	5.6060	5.6060	5.606	5.606	5.606
Thiosulphate left as (S_2O_3'') ..	5.33093	5.16836	4.62472	3.42502	2.0068
Thiosulphate decomposed as (S_2O_3'')	0.27507	0.43764	.98128	2.18098	3.59920
Sulphate formed as $BaSO_4$ ..	0.2300	0.5500	1.2650	2.6200	3.9000
Sulphate formed as SO_4'' ..	0.09465	0.22634	0.5200	1.07822	1.60498

First Stage : To start with, medium of the reaction was alkaline, therefore, the oxidation of sulphide solution took place with the formation of thiosulphate (S_2O_3''), a product which is in the lower state of oxidation, because the oxidising power of nitric oxide (and also that of other oxidising agent) is low in the alkaline medium (due to the low oxidising potential).

Sodium hydrosulphide produced from the reaction (1) reacted with nitric oxide to give thiosulphate according to the equation :

$$4NaHS+10NO=2Na_2S_2O_3+2N_2O+2H_2O+3N_2 \quad .. \quad (2)$$

This change was also confirmed by the analysis of the gaseous products of the reaction, where nitrous oxide and nitrogen were obtained. Nitric oxide on long contact with water gave

nitro-hydroxylammic acid (Angeli's acid).[18] This acid reacted with sodium hydrosulphide according to the equation

$$4NaHS+5H_2N_2O_3=2Na_2SO_4+2S+7H_2O+5N_2 \quad .. \quad (3)$$

Second Stage : The sulphur which was set free during the first stage of the reaction combined with the unreacted sulphide to give polysulphides.

$$Na_2S+S=Na_2S_2 \quad .. \quad (4)$$
$$Na_2S_2+S=Na_2S_3 \quad .. \quad (5)$$

Third Stage : Due to the greater dissolution of nitric oxide in solution, the medium became less alkaline consequently the thiosulphate was decomposed by nitric 'oxide according to the equation :

$$2Na_2S_2O_3+2NO=2Na_2SO_4+2S+N_2 \quad .. \quad (7)$$

During the initial stages nitrogen and nitrous oxide (cf. equation (2) above) were present as the gaseous products of the reaction, but towards the final stage nitrogen was the only product formed.

Fourth Stage : Sulphide, polysulphide and thiosulphate were completely decomposed to give sulphate and sulphur. The total reaction under all the four steps above may be summed up as follows :—

$$4NaHS+10NO=2Na_2SO_4+5N_2+2S+2H_2O \quad .. \quad (8)$$

This equation is based on the quantitative data recorded in tables 1 to 4 where it has been shown that half the amount of sulphur accounted from sulphide was precipitated as free sulphur, while the remaining half was present in the sulphate formed at the final stage of oxidation. The analysis of the gaseous products at various stages indicated that nitric oxide was ultimately reduced to nitrogen though initially nitrous oxide was also formed as an intermediate product.

The course of reaction as studied in the case of sodium disulphide was found to be identical with that in the case of mono-sulphide except that the quantity of the various products formed was higher due to the presence of greater amount of sulphur in the compound. However in the case of the trisulphide, some deviations from the usual course of reaction were observed.

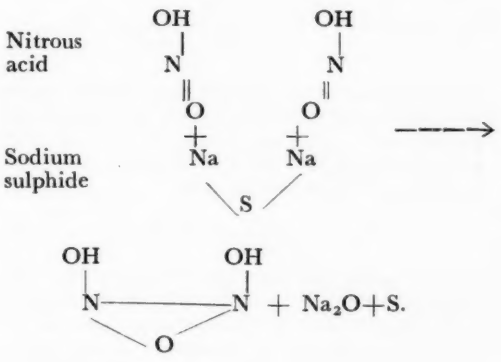
Reaction Mechanism

The by-product such as nitrite and ammonium ions were also studied in order to ensure their formation and to elucidate the mechanism of the reaction.

According to L. Moser, [19] F. J. Joss,[20] and S. Zimmermann[21] nitric oxide cannot be preserved over water without any change owing to the hydrolysis :

$$4NO+H_2O=2HNO_2+H_2N_2O_2 \quad (9)$$

Zimmerman[21] also said that nitric oxide on long contact with water gives nitro-hydroxylaminic acid (Angeli's acid). The formaton of Angeli's acid from nitrous acid and Na_2S can be explained as below :—

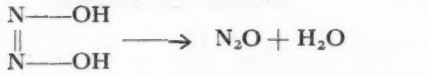


(Angeli's acid) (10)

This acid then reacted with NaHS to give hyponitrous acid which decomposed to give nitrous oxide and H_2O.

$$NaOH+S+\begin{matrix}N-OH\\ \|\\ N-OH\end{matrix} \quad (11)$$

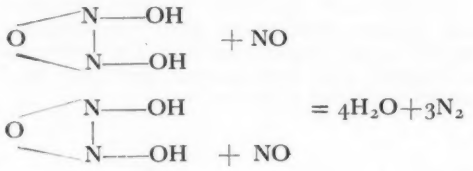
(hypo-nitrous acid)



$$N_2O + H_2O \qquad (12).$$

It appears that the starting point in the whole mechanism is hyponitrous acid and nitrous acid.

With the passage of time the quantity of Angeli's acid increased with the result that it started decomposing gradually as shown by the equation:

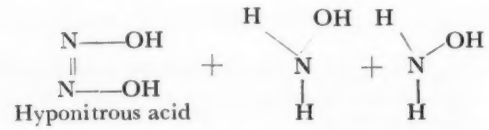


$$= 4H_2O + 3N_2 \qquad (13)$$

The evidence of the hydration of nitrous oxide to give hyponitrous is also given by Nichols and Derbigney.[22] The mechanism of the final product of reduction is thought to depend upon the formation of hyponitrous acid.

$$N_2O + H_2O = (NOH_2)_2 \qquad (14)$$

(Hyponitrous acid has been discussed by L.H. Milligan and G.R. Gillete,[23] W.D. Bancroft,[24] N.R. Dhar,[25] and M. Coblens and J.K. Berstein.[26]) Accordingly the formation of nitrogen in the final stage of oxidation can be explained by



$$= 2N_2 + 4H_2O \qquad (15)$$

The formation of nitrite can be explained thus :—

$$4NO + 2NaOH = N_2O + 2NaNO_2 + H_2O \qquad (16)$$

In the beginning of the experiment, the nitrite was in excess but its amount decreased later as the medium became less alkaline.

The formation of ammonium can be explained by the reaction :

$$HNO_2 + 3S = NH_4 + H_2O \qquad (17)$$
(polysulphide)

Towards the end interaction takes place and N_2 is produced according to the equation :

$$NH_4 + NO_2 = 2H_2O + N_2 \qquad (18)$$

Nitrous oxide also reacts with NH_3 to give nitrogen.

$$2NH_3 + 2N_2O = 4N_2 + 3H_2O \qquad (19)$$

To sum up, the above experiments lead us to the conclusion, that sodium sulphide is oxidised by nitric oxide to give sulphate and sulphur in the final stage of the reaction through the intermediate formation of polysulphides, thiosulphate, a small amount of NH_4^+ and NO' ions. Nitric oxide is reduced to nitrogen via nitrous oxide. Sulphate is virtually the end product in solution, sulphur in the precipitate, and nitrogen in the gaseous products of the reaction, thus

$$NaHS + 10NO = 2Na_2SO_4 + 5N_2 + 2H_2O. \qquad (20)$$

References

1. Milligan, J. Phys. Chem., **33**, 1335, (1929).
2. J. Priestly, *Experiments and observations on different kinds of Air*, London 1774, Burmingham, 1., 328, 1790, 211.
3. H. Davy, *Researches Chemical, Philosophical, Chiefly concerning Nitrous oxide or Dephlogisticated nitrous air and its Respiration* London, 1800.
4. Leconte, Ann. Chim. Phys., (3), **21**, 180.
5. Trautz and Volkman, Zeit. Phys. Chem., **64**, 1 (1908).
6. P. Pauli, Chem. News, **5**, 80 (1862).
7. Mourlot, Ann. Chim. Phys., **7**, 510.
8. A. Klemenc, Montash, **58, B,** 492 (1925).
9. Dunnicliff, Sardar Mohammad and Jai Kishan., J. Phys. Chem., **35**, 1721-1734 (1931).

10. Dunnicliff and Kotwani, J. Phys. Chem., **35**, 3215 (1931).

11. Dunnicliff and Soni, J. Phys. Chem., **33**, 81 (1929).

12. J.A. Pierce, J. Phys. Chem., **33**, 22 (1929).

13. Dunnicliff, Sardar Mohammad and Jai Kishan, Referred above vide 9.

14. Badar-ud-Din and Riaz-ur-Rehman, Pak. Jr. Sci., **5**, 2 (1953).

15. Badar-ud-Din and Riaz-ur-Rehman, Pak. Jr. Sci., **5**, 2 (1953).

16. Dunnicliff, S. Mohammad and Jai Kishan, J. Phys. Chem. **35**, 1727 (1931).

17. —do— (Already referred).

18. Angeli, Fazz, 26 II, 245 (1877), Angelo and Angelo Co : 3311, 245 (1903).

19. L. Moser, Zeit, Anal, Chem., **16**, 36, 438 (1903).

20. F.J. Joss, J. Phys. Chem. Soc., **32**, 35 (1877).

21. S. Zimmermann, Mongtschafte, 26, 277 (1893).

22. Nichols and Derbigney, J. Phys. Chem., **30**, 491 (1926).

23. L.H. Milligan and W.R. Gillete, J. Phys. Chem. **28**, 544 (1924).

24. W.D. Bancroft, J. Phys. Chem. **28**, 744 (1924).

25. N.H. Dhar, J. Phys. Chem., **29**, 142 (1929).

26. M. Coblens and J.K. Berstein, J. Phys. Chem., **20**, 491 (1925).

RADIO FREQUENCY TRANSMISSION SYSTEM A 30 MEV ELECTRON CYCLOTRON

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THE principle of magnetic resonance in which the operation of an electron cyclotron rests has been discussed in great detail by various authors since its introduction by Veksler (Veksler,[1] Readhead et al.,[2] Henderson et el.,[3] Itoh and Kobayshi[4]). It consists essentially of a resonant cavity situated in a uniform magnetic field. The cavity is energized by a pulsed magnetron.

A very high electric field is obtained across the lips of the cavity. The electrons obtained by field emission from the lips of the cavity and accelerated each time they pass through the cavity describe orbits of increasing radius which all have a common tangent through the resonator.

The radio frequency system of the electron cyclotron consists mainly of three parts : (a) the R.F. source ; (b) the R.F. transmission system ; and (c) the cavity resonator.

The R.F. source is a high power pulsed magnetron with a conventional modulator unit. This paper describes the development and design of an efficient R.F. transmission system for feeding power stably from the magnetron to the cavity resonator.

Magnetron Stabilization

If the magnetron is coupled to a waveguide terminated in a resonant load the input impedance under cold condition may be represented by

$$Y_L(w) = G(w) + jB(w) \quad - - - (1)$$

where (w) is the angular frequency, G(w) represents the conductance and B(w) the susceptance. G(w) and B(w) can be determined in terms of the admittances of the magnetron cavity and load and the waveguide constants.

Fig. (1) shows B(w) as a function of G(w) at different frequencies in the complex plane. $Y_L(w)$ at any frequency can be found from this curve.

When the magnetron is under operating conditions, new admittances are introduced

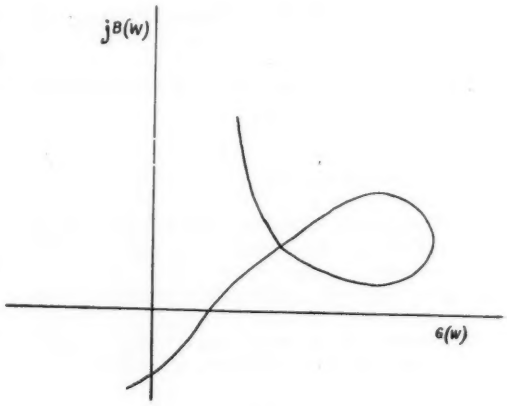


Fig. 1

due to electron loading in the magnetron. We represent this admittance as Y_e. When $Y_e = -Y_L$ the total input admittance of the magnetron is zero and this is the condition for maintaining oscillations. The admittance Y_e depends on the voltage and current applied to the electron stream and other input states such as temperature, etc. We shall assume that the Y_e curves are straight horizontal lines parallel to the real axis, when represented in the G-B plane. In general, Y_e curves may intersect the Y_L curves at more than one point, indicating that $Y_L = -Y_e$ at more than one frequency, and the magnetron is capable of oscillating at more than one frequency not all of them, however, are stable. In practice, the magnetron does not oscillate at two frequencies simultaneously. This must mean either that there is involved some sort of selection process which operates in favour of one or the other of the intersections or that simultaneous oscillation at two frequencies is an inherently unstable state.

The most natural way to describe the operation of a magnetron is in terms of its Ricke diagram, which is a plot on a circle impedance diagram of its performance (output power and frequency) for loads of all possible impedances. If the load is critical to frequency, as in the case of a resonant cavity and if its impedance is plotted as the frequency is varied,

a curve will be obtained on the chart. Possible operating points, if any, will be at points where the magnetron frequency contours intersect the load curve at their own frequency.

When the magnetron is switched on, there is nothing to choose between the various possible modes, and they will all be present at very low amplitude. Due to the non-linear characteristics of the oscillator, the operating condition with the most rapid rate of build-up of oscillation will be the one in which the steady-state is reached, to the exclusion of all other modes. The mode of most rapid build-up is normally that of lowest equivalent Q-factor.

Unfortunately the build-up of oscillation at the resonant frequency of the cavity has the slowest rate.[5] If other modes are possible, oscillation will not take place at the resonant frequency, hence if operation is desired at the resonant frequency, it must be the only mode which fulfils the stability requirements. The method of suppressing the unwanted modes is to ensure that both the admittance and the impedance of the load remain less than certain critical values dependent on the characteristics of the oscillator at frequencies remote from the resonant frequency of the load. In other words, it is necessary to dissipate some of the power in a load so that the resonance curve is displaced towards the centre and made symmetrical with respect to the magnetron frequency contour equal to the resonant frequency of the cavity. There are several methods by which this can be done ; we shall discuss two of them which are most practical :

(1) A resistive load is inserted either in series with the transmission line at an integral number of half-wavelengths from the resonator input, or in parallel at an odd number of quarter-wavelengths from the resonator. The minimum value of this load depends largely on the character of the Ricke diagram of the oscillator. The arrangement is called 'point load stabilization'.

(2) An attenuator with some suitable transformer is inserted in the transmission system. The arrangement is called 'attenuator load stabilization'.

Point Load Stabilization

For mechanical reasons, the stabilizing load is placed in series with the transmission line at an integral number of half-wavelengths from the resonator input. This is done by coupling the stabilizing load to the main wave-guide through an E-plane series T-junction. In such a junction, the discontinuities in the guide give rise to storage fields, the effects of which may be represented by lumped susceptances. The numerical values can be determined from the wave-guide dimensions, using the empirical information collected by Huxley.[6] The stabilizer resistor is a matched water load. The inductive susceptances in the main arms of the T-junction are considered to be small enough not to require compensation. Two appropriately placed screws ahead of the water load can be used to adjust the load to its optimum value and to cancel the shunt susceptance at the side-arm introduced into the wave-guide by the T-junction. Figure 2 shows the layout of the stabilizer. The whole stabilizer system can be represented as a damping resistor in series with the cavity. The cavity plus this resistor now represents the load.

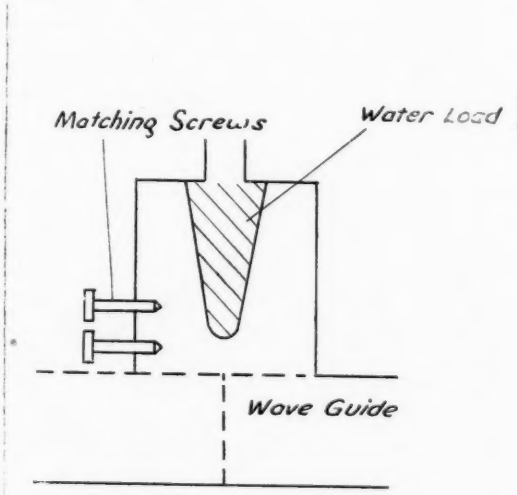


Fig. 2

The effect of the damping resistor in suppressing the extraneous modes can be analyzed by means of admittance curves in a reflection coefficient diagram (Smith chart) which are called circle diagrams. If the off resonance region of circle diagram of the cavity plus stabilizing resistor is sufficiently displaced towards the centre of the Smith chart there will be one and only one operating point which can be adjusted to be at the resonant frequency of the cavity. In addition it is advantageous to arrange for the circle diagram to be symmetrical with respect to the centre of the impedance diagram, since then the magnetron

would operate into a load of constant voltage standing wave ratio irrespective of misadjustment of the resonator frequency.

Circle diagram of point-load plus loaded cavity:

Let R_s = Series resistance introduced by point load.

R_c = Cavity shunt resistance.

Z_o = Characteristic impedance of waveguide.

$$R_1 = \frac{R_s}{Z_o} \text{ and } R_2 = \frac{R_c}{Z_o}$$

on-tune V.S.W.R., $S_o = R_1 + R_2$.

on-tune reflection coefficient,

$$P_o = \frac{R_1 + R_2 - 1}{R_1 + R_2 + 1}$$

Off-tune reflection coefficient,

$$P_{off} = \frac{R_1 - 1}{R_1 + 1}$$

Circle diagram of point load plus unloaded cavity:

Let R_E = Shunt resistance introduced due to electron beam loading in the cavity

and $f = \frac{R_c}{R_E} = \frac{\text{Beam power}}{\text{Wall losses}}$

on-tune reflection coefficient,

$$P_{ol} = \frac{(R_1+R_2-1)+f(R_1-1)}{(R_1+R_2+1)+f(R_1-1)} \quad (2)$$

off-tune reflection coefficient,

$$P_{ofl} = P_{off} = \frac{R_1-1}{R_1+1}$$

Circle diagrams of point load plus loaded and unloaded cavity are drawn in Fig. 3.

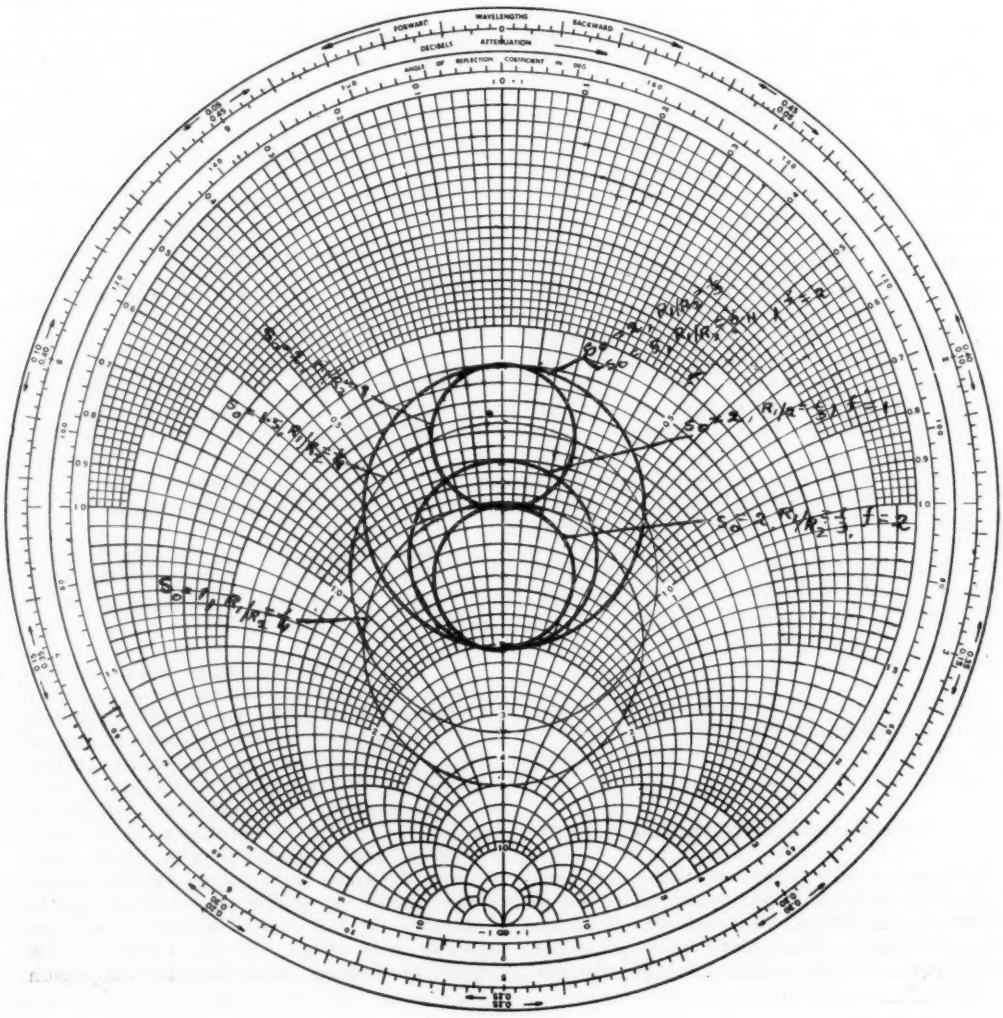


Fig. 3

Power relations in a point load stablizer system

Power dissipated in resonator and electron beam

$$= V_R^2 \frac{(R_E+R_C)}{R_E R_C}$$

Resultant input power

$$= V_R^2 \frac{(R_C+R_E)}{(R_C R_E)^2} \quad (R_C R_E + R_S R_C + R_E R_S)$$

put $$f = \frac{R_C}{R_E} = \frac{\text{Power in beam}}{\text{Power in resonator walls}}$$

and $$F = \frac{\text{Input power}}{V_R^2/R_C} = \frac{\text{Input power}}{\text{Power in resonator walls}}$$

Then $$F = \left[f+1\right]\left[1+\frac{R_S}{R_C}(1+f)\right] \quad .. \quad .. \quad (3)$$

Normalizing R_S, R_C and R_E we get

$$R_1 = \frac{R_S}{Z_0} \quad R_2 = \frac{R_C}{Z_0} \quad R = \frac{R_E}{Z_0}$$

and

$$F = (f+1)\left\{1+R_1/R_2\,(1+f)\right\} \quad .. \quad .. \quad (4)$$

Groups of F v s f for point load system are shown in Fig. 4.

Attenuator—load stabilizer

Theoretical analysis: The general arrangement of the R.F. transmission system with the attenuator load is shown in Fig. 5 and the equivalent circuit is shown in the inset to Fig. 5.

We shall consider the circle diagrams as measured at terminals C-C (Inset Figure 5). The quarter-wave transformer is of characteristic impedance r_0. The attenuator has the same characteristic impedance Z_0 as the

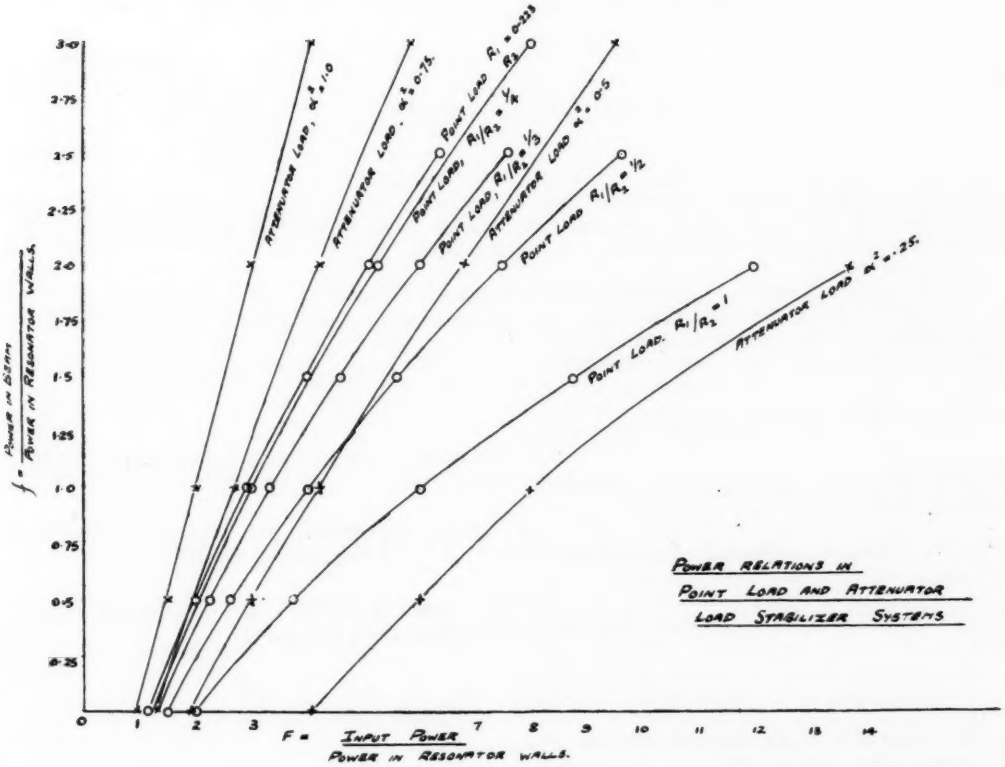

f = Power in Beam / Power in Resonator Walls.
F = Input Power / Power in Resonator Walls.
Attenuator Load, α² = 1.0
Attenuator Load, α² = 0·75.
Point Load R₁ = 0·333 R₂
Point Load, R₁/R₂ = ¼
Point Load, R₁/R₂ = ⅓
Attenuator Load α² = 0·5
Point Load R₁/R₂ = ½
Point Load. R₁/R₂ = 1
Attenuator Load α² = ·25.
Power Relations in Point Load and Attenuator Load Stabilizer Systems

Fig. 4

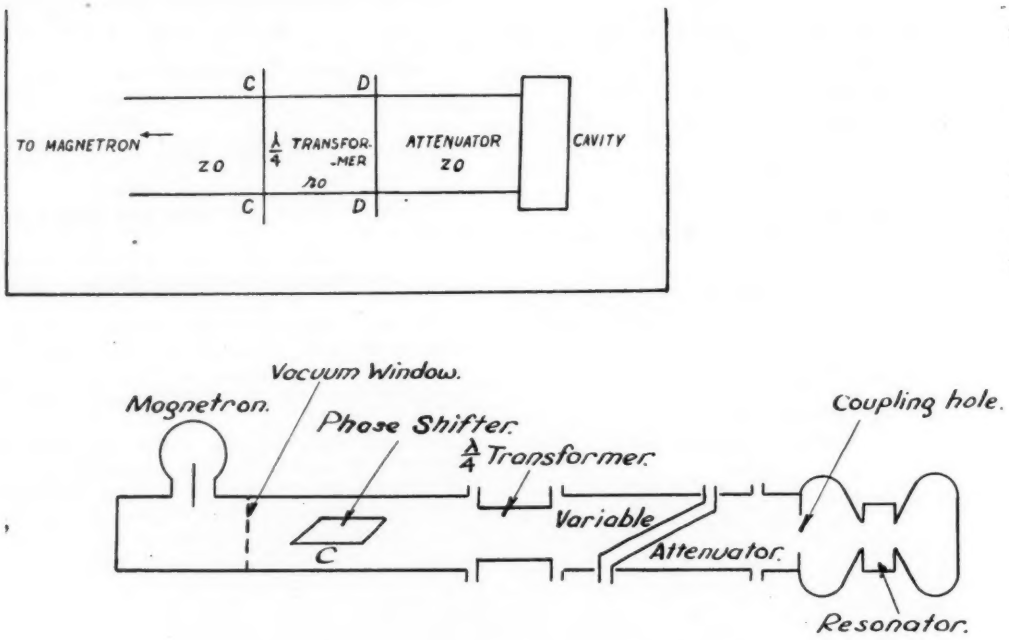


Fig. 5. R. F. Transmission system

waveguide and is an integral number of half-wavelengths. Let the attenuator reduce the field in passing through it by a fraction α.

Let the on-tune reflection coefficient for the unloaded cavity be P_o. Assuming no phase change by the attenuator, the on-tune reflection coefficient at the attenuator input $= \alpha^2 P_o$.

On-tune V.S.W.R. at attenuator input $= \dfrac{1-\alpha^2 P_o}{1-\alpha^2 P_o}$

Off-tune reflection coefficient at unloaded cavity $= -1$

Off-tune reflection coefficient at attenuator input $= -\alpha^2$

Off-tune V.S.W.R. with no load at attenuator input

$$= \frac{1-\alpha^2}{1+\alpha^2}$$

As the attenuator is an integral number of half-wavelengths, the on-tune input impedance at attenuator input (Terminals D-D) is R_C and the off-tune impedance is jx_C (neglecting change in electrical length due to change of frequency.

On-tune V.S.W.R. at attenuator input if there were no transformer

$$S_o = \frac{1+\alpha^2 P_o}{1-\alpha^2 P_2}$$

Off-tune V.S.W.R. at attenuator input without transformer

$$S = \frac{1-\alpha^2}{1+\alpha^2}$$

On tune V.S.W.R. at transformer input (Terminal C-C) is given by

$$S_{on} = \frac{r_o^2}{Z_o^2 S_o} = \frac{n^2}{S_o}$$

where $n = \dfrac{r_o}{Z_o}$

Off-tune V.S.W.R. at transformer input is given by

$$S_{of} = \frac{Z_o^2 S}{r_o^2} = \frac{n^2}{S}$$

On-tune reflection coefficient at transformer input

$$P_{on} = \frac{\frac{n^2}{S_o^2} - 1}{\frac{n^2}{S_o^2} + 1} = \frac{(n^2-1) - \alpha^2 P_o (n^2+1)}{(n^2+1) - \alpha^2 P_o (n^2-1)} \quad \ldots (5)$$

Off-tune reflection coefficient at transformer input

$$P_{off} = \frac{\frac{n^2}{S} - 1}{\frac{n^2}{S} + 1} = \frac{(n^2-1) + \alpha^2 (n^2+1)}{(n^2+1) + \alpha^2 (n^2-1)} \quad \ldots (6)$$

we have $P_o = \frac{R^2-1}{R^2+1}$ for unloaded cavity

$$P_{lo} = \frac{2P_o - f(1-P_o)}{2 + f(1-P_o)}$$ for loaded cavity

In this analysis we are assuming that the electrical length of the attenuator remains constant at an integral number of half-wavelengths, while the transformer remains quarter-wavelengths over the whole frequency range. This is nearly true since we are dealing with a small frequency range. If the length of the attenuator is not an integral number of half-wavelengths the circle diagram will be rotated bodily and some deformation of the curve from its circular form, which is not at all serious for practical purposes, will result. The circle diagram can, however, be brought back to its original position by means of some suitable phase shifter introduced into the transmission system.

Circle diagrams for attenuator load system plus cavity are shown in Fig. 6.

Power relation in an attenuator load stabilizer system.

Power input varies as $(1 - P^2 \alpha^4)$

where P is the reflection coefficient at cavity input.

At resonant frequency total power absorbed by resonator varies as

$\alpha^2 (1 - P^2_{LO})$

Resonator power division

$$\frac{P_{beam}}{P_{wall}} = \frac{\text{Power in Beam}}{\text{Power in Wall}} = f$$

$P_{wall} + P_{beam}$ varies as $\alpha^2 (1 - P^2_{LO})$

or, $$1 + f = \frac{\alpha^2 (1 - P^2_{LO})}{P_{wall}}$$

or, $$P_{wall} = \frac{\alpha^2 (1 - P^2_{LO})}{1 + f}$$

$$\frac{\text{Power input}}{\text{Power in Wall}} = F = \frac{(1 - P^2_{LO} \alpha^4)\ (1 + f)}{\alpha^2 (1 - P_{LO}^2)} \quad (7)$$

Graphs of F V S f are also shown in Fig. 4.

Discussion of results and comparison of the performance of the two systems : The study of the circle diagrams in Figure 3 reveals that the point load stabilizer system with an unloaded cavity has a symmetrical circle diagram for $R_1/R_2 = 1/3$ with $R_2 = 1.5$ and the V.S.W.R. as seen by the magnetron is 2 at all frequencies. When the cavity is loaded with $f = 2$ off-tune standing wave ratio remains the same ; but the on-tune standing wave ratio is considerably reduced.

A slightly better circle diagram (Figure 6) is given by the attenuator system with unloaded cavity for $\alpha^2 = 0.5$, with $R_2 = 1.5$ and $n^2 = 0.64$ and the V.S.W.R. is nearly 1.9 at all frequencies. Keeping the off-tune V.S.W.R. the same, the cavity loading again reduces the on-tune V.S.W.R. The circle diagrams illustrate the point that any circle diagram which can be produced by a point load system can also be produced by an attenuator system by a proper choice of the attenuation and the quarter-wave transformer.

The study of Figure 4 shows that for values of beam loading in accelerator cavity upto about three times the wall losses the circuit efficiency is slightly better in the point load system than in the attenuator system. Normally, the beam loading is twice the resonator wall losses and hence the point load system compares favourably with the attenuator system so far as power relations are concerned. This slight advantage in power relations in the point load system, is however more than offset by difficulties in its design and operation. It is not possible to compensate all the reactances and susceptances associated

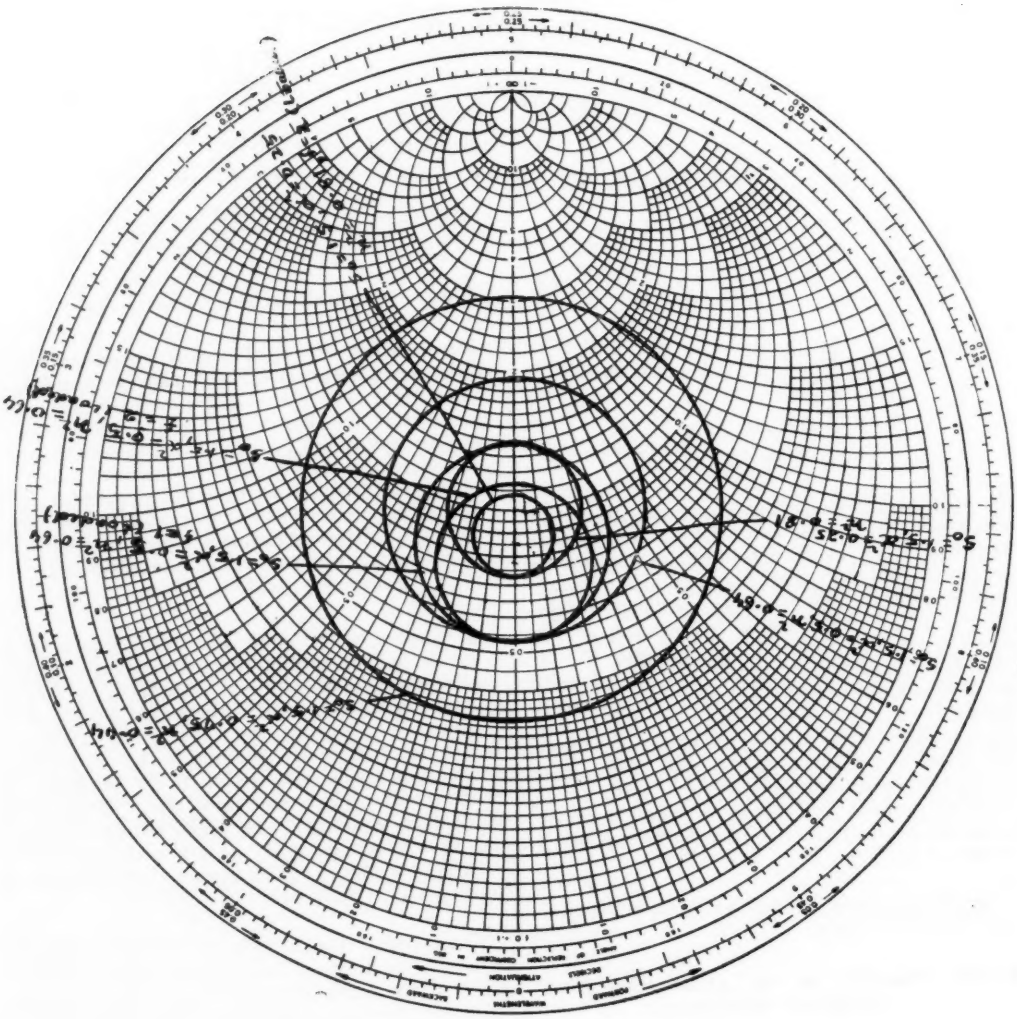


Fig. 6

with the point load, nor is it possible to *continuously* vary this load for operational adjustments. Moreover, we do not know the Ricke diagram of the magnetron. If we use a point load, we have to guess the minimum value of the stabilizing resistor, and we will almost certainly make it too large in order to be on the safe side.

An attenuator can, however, be easily designed and constructed with means of adjustments during operation.

Attenuator Load

A variable evacuated attenuator load was designed and constructed in the laboratory and its performance was studied experimentally with a view to using it in an attenuator transmission system in the electron cyclotron. The general arrangement of the attenuator load is shown in Figure 7 and Plate I. It is a variable

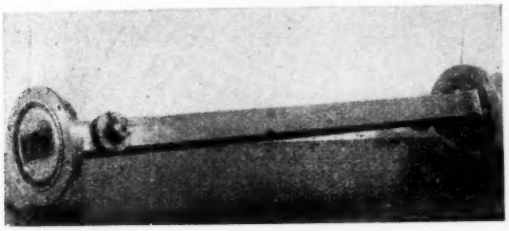
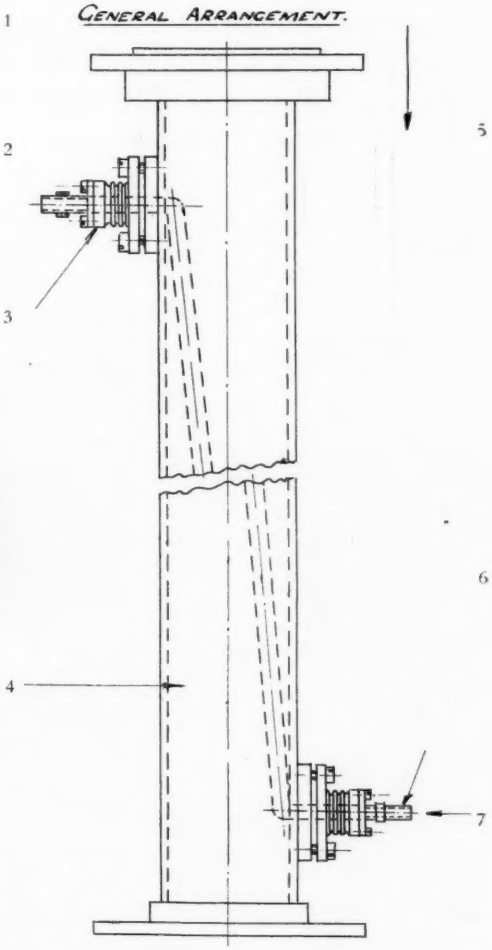


Plate 1

water load attenuator with a glass tube passing through a wave-guide at a slanting angle. The attenuation is varied by varying the level of water inside the tube as shown diagrammatically in Figure 8.

The glass tube is bent at right angles at both ends, which come out of the waveguide through two vacuum-sealed assemblies on top and bottom faces of the waveguide. Water is slowly dripped in from water mains to the top end of the glass tube and comes out through the bottom end, which is connected to one end of a rubber tube, the other end of which carries a glass tube placed vertically along a millimetre scale to read its top head. By sliding the glass tube up and down the water level inside the waveguide can be adjusted.

Attenuation was measured for different water levels inside the attenuator by the standing wave ratio method. The circle diagrams of the attenuator terminated by the cavity for different attenuation constants were also determined from the standing wave



1 Water Load
2 Variable Attenuator
3 Outlet Assembly
4 Wave-guide
5 Power In
6 Glass Tube
7 Water In

Fig. 7

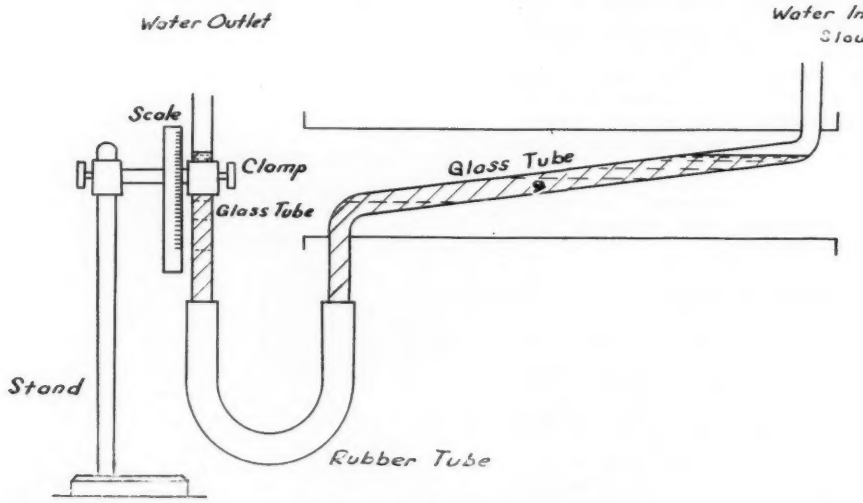


Fig. 8.—Schematic diagram of variable water load attenuator.

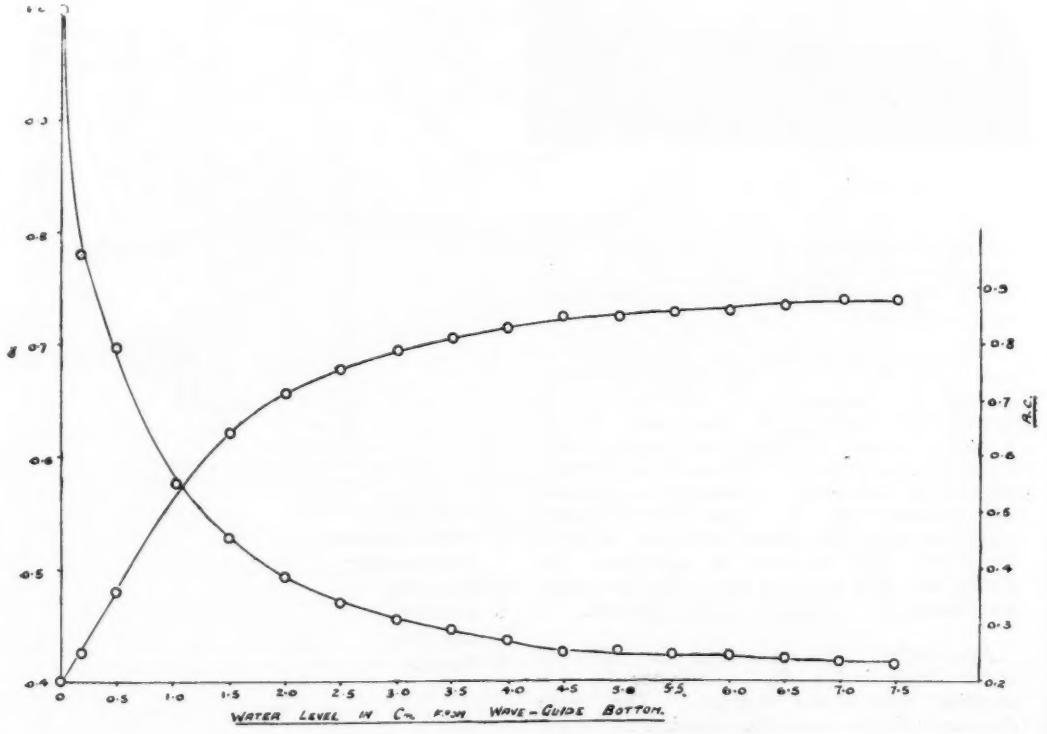


Fig. 9.—Attenuation of water load attenuator.

measurements. The results of measurements are shown in Figs. 9, 10(a) and 10(b).

The variation of attenuation with water level in the glass tube inside the attenuator was very smooth as shown in Fig. 9. The water had to be slowly dripped and care was taken to drive out any air bubbles in the water column inside the attenuator. The attenuation was dependent slightly on the frequency. This was due to the very broad resonance characteristics of a long waveguide. The reflection of electromagnetic waves from the attenuator was negligible.

The circle diagrams of the attenuator terminated by the cavity are given in Figs. 10(a) and (b) for $\alpha^2=0.25$, 0.5 and 0.75 respectively. These diagrams could easily be made symmetrical with respect to the centre of the impedance chart by putting a suitable quarter-wave transformer at the input of the attentuator. The circle diagram for $\alpha^2=0.5$ or $\alpha^2=0.75$ would be quite good, when made symmerrical for stabilization of magnetron frequency. Under this condition one-third of the input power would be dissipated in the attenuator which might be considered quite reasonable. The circle diagram for $\alpha^2=0.25$ or $\alpha^2=0.5$

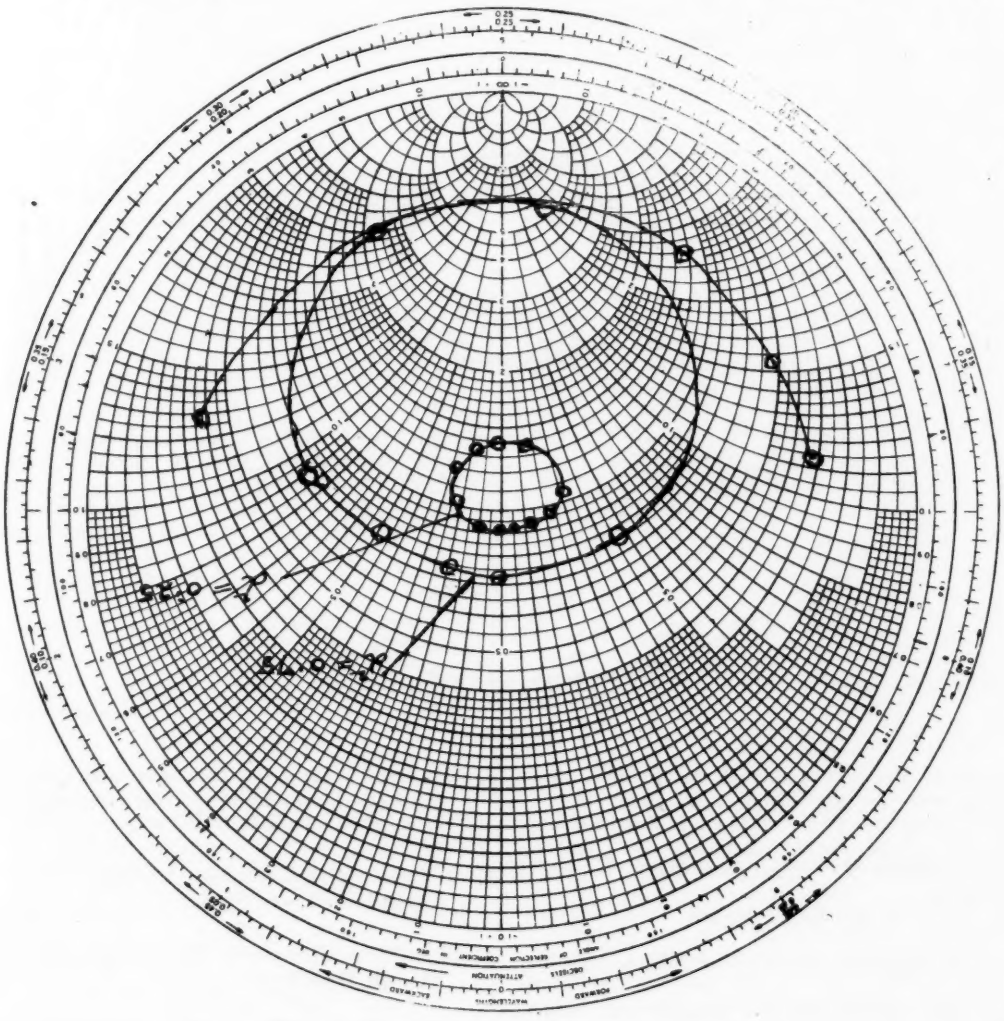


Fig. 10 (a)

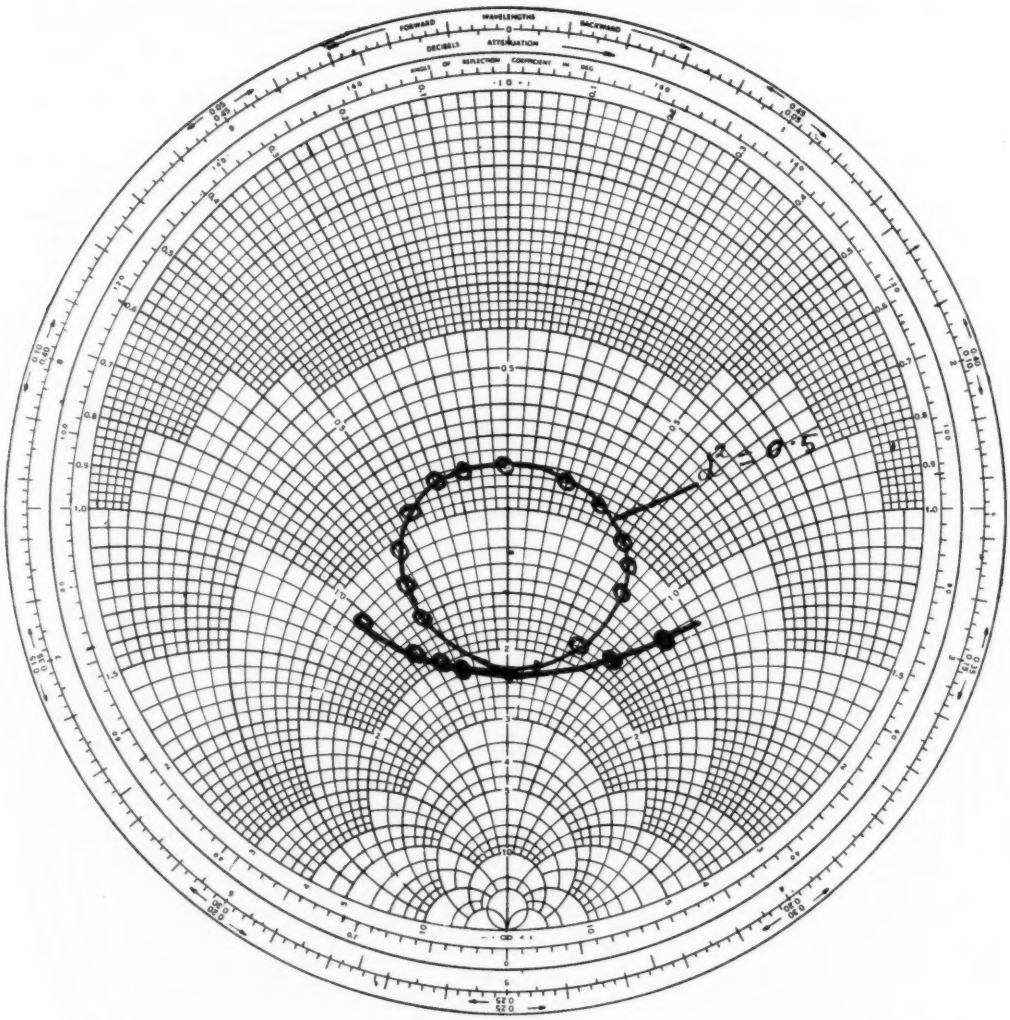


Fig. 10 (b)

would be the best so far as stabilization was concerned. In the latter case power dissipated would be 50%. The circle diagram for $\alpha^2=0.75$ could not be accepted, for under this condition the magnetron might become unstable.

References

1. V. Veksler, J. Physics U.S.S.R. **9** (1945).

2. P.A. Readhead, H. Lecaine and W.J. Henderson, Canadian Journal of Research, A, **28** (1950).

3. C. Herderson, F. F. Heymann and R.E. Jennigus, Proc. Phy. Soc. **66B, 41** (1953). Proc. Phy. Soc. **66B,** 654 (1953).

4. I. Itoh and D. Kobayashi, Co. Fac. Sci., Osaka Uni. B. **11** (1950).

5. B.Y. Mills, Proc. Inst. Elect. Engg. Part III, **97,** 425 (1950).

6. L.G. Huxley, *Wave-guides* (Cambridge 1947).

SCATTERING OF HIGH ENERGY ELECTRONS IN NUCLEAR EMULSION

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DURING the last few years the photographic emulsion technique has been applied to a wide variety of problems concerning nuclear studies. As far as the author is aware there have been no previously published investigations of electron-electron scattering using this technique. However, soon after the present work was started some work of Barkas et al.[1] from Berkeley using this technique for the study of positron electron scattering was published. This is perhaps surprising since the study of delta rays (*i.e.*, electrons with small fractional energy loss) has in recent years been applied frequently to the identification of particles in photographic emulsion.

The photographic emulsion methods are useful because they provide permanent records of the tracks of fast electrons and all the details of collision processes can be studied carefully at leisure. Since the electron density in the material of the emulsion is comparatively well-known it is possible to obtain unambiguous results of the collision cross-sections in this case. It was, therefore, decided to use the emulsion technique to study electron-electron scattering.

The method enables one to obtain results in the case of collisions involving small fractional energy losses of the incident electrons. It would be interesting also to obtain results for larger fractional energy losses but such events are rare and, therefore, the statistical uncertainties in the observed values are high. Nevertheless, the previous work on electron-electron scattering is so meagre and confined to so few incident-electron energies that it seemed worthwhile to carry out the present investigations inspite of the limitation to rather small energy losses. A short note on the present work was published earlier.[2]

Theory

The most rigorous treatment of the problem of electron-electron collision is due to Moller.[3] His formula for the cross-section of the scattering per electron between angles θ^* and $\theta^* + d\theta^*$ (in the centre of mass system) is

$$\sigma(\theta^*)\,d\theta^* = \frac{(\gamma+1)\pi r_o^2 \operatorname{Sin}\theta^* d\theta^*}{\gamma^2\beta^4}\left[\operatorname{Cosec}^4\theta^*/_2 + \operatorname{Sec}^4\theta^*/^2 - \operatorname{Cosec}^2\theta^*/_2 \operatorname{Sec}^2\theta^*/_2 + \left(\frac{\gamma-1}{\gamma}\right)^2(1+4\operatorname{Cosec}^4\theta^*)\right] \ldots\ldots(1)$$

where r_0 is the classical electron radius, $\beta = v/c$ and $\Upsilon = \frac{1}{\sqrt{1-\beta^2}}$ = total energy (kinetic + rest mass) of the incident electron in units of m_0c^2, the rest mass energy of the electron. The first two terms within the bracket correspond to the relativistic Rutherford formula. The third term is the quantum mechanical exchange term. The inclusion of this term in the relativistic Rutherford formula gives the relativistic Mott[4] or the Kar and Basu[5] formula. The fourth term accounts for the retardation effect and its inclusion in the relativistic Mott or the Kar and Basu formula gives the Moller formula. This term, however, vanishes in the non-relativistic limit $\Upsilon \to 1$.

The formula, according to Moller, may be expressed in terms of a new variable A, the ratio of the kinetic energy of the knock-on electron to the kinetic energy of the incident electron. By a simple transformation the Moller formula (1) may be written as

$$\sigma(A)dA = \frac{2\pi r_0^2}{\beta^2(\gamma-1)}\left[\frac{1}{A^2(1-A)^2} - \frac{3}{A(1-A)} + \left(\frac{\gamma-1}{\gamma}\right)^2\left\{1+\frac{1}{A(1-A)}\right\}\right]dA \ldots\ldots(2)$$

The relativistic Rutherford formula in the same notation is

$$\sigma(A)dA = \frac{2\pi r_0^2}{\beta^2(\gamma-1)}\left[\frac{1}{A^2(1-A)^2} - \frac{2}{A(1-A)}\right]dA \ldots\ldots\ldots(3)$$

The relativistic Mott or the Kar and Basu formula is

$$\sigma(A)dA = \frac{2\pi r_0^2}{\beta^2(\gamma-1)}\left[\frac{1}{A^2(1-A)^2} - \frac{3}{A(1-A)}\right]dA \ldots\ldots(4)$$

Technique and Measurements

(*a*) *Exposure of plates :* Ilford G5 plates of dimensions $2'' \times 2''$ and emulsion thickness 200 microns were exposed to electrons accelerated to high energies by a 20-MEV synchrotron at the University College, London. The plates were then processed by the so-called "temperature development" method of Dilworth et al.[6]

*The experimental part of the work described here was done at the University College, London, while holding an 1851 Exhibition Scholarship.

(*b*) *Measurements :* Measurements of the plates were carried out using a Beck binocular microscope. A 2 mm (~ 80 x) oil immersion objective was used in conjunction with 15 x compensated eyepieces fitted with a calibrated scale (1 division = 0.635μ) and a protractor provided with a vernier (1 division = 10 minutes).

The plates were mounted on the mechanical stage of the microscope in such a way that the tracks were approximately parallel to the y-axis of the stage motion. The tracks, which started right from the surface of the emulsion were followed by advancing the stage of the microscope by means of the screws, and the length traversed by the electron was read on the vernier scale of the stage. 90 cm. of track were scanned at each incident energy *viz.* 6.5, 11.5 and 18.7 MEV.

Whenever an electron-electron collision was observed, both the range of the knock-on electron and the angle between its direction and that of the incident electron were measured, wherever possible. These measurements were made by means of the calibrated scale and the protractor, respectively. For very low energy knock-ons the angle became very difficult to measure because of strong nuclear scattering. Therefore, the range was the principal means of determining the energy of the knock-on electron upto about 0.5 MEV. It was, however, observed that most of the recoil electrons with energies greater than 0.2 MEV went out of the emulsion. For the higher energies, therefore, we had to depend on the angle measurements only. Very good agreements were observed when both measurements were possible on individual tracks.

The true length, L, of the recoil track is given by

$$L^2 = l^2 (1 + \tan^2\beta) \quad \ldots\ldots(5)$$

where l is the projected length of the recoil track and β, the angle of dip. The energy of the recoil electron was then found out from the range-energy relation of electrons for photographic emulsion, as has been measured by Zajac and Ross.[7]

The true angle, Φ, which the recoil electron makes with the incident electron is given by

$$\cos\Phi = \cos\alpha \cos\beta \quad \ldots\ldots(6)$$

where α is the angle of ejection projected on the plane of emulsion containing the incident electron and β the dip angle. The energy, Q, of the recoil electron was then calculated from the angle-energy relation

$$Q = \frac{E \cos^2\Phi}{1 + \frac{E \sin^2\Phi}{2 m_0 c^2}} \quad \ldots\ldots(7)$$

where E is the energy of the incident electron and m_0c^2 the rest mass energy of the electron.

Results

(*a*) *Calculation of theoretical cross-section :* Calculations of the theoretical cross-sections have been carried out by integrating the differential cross-sections given by equations 2, 3 and 4. After integrations are carried out, the three equations become

Rutherford :

$$\int \sigma(A)\, dA = \frac{2\pi r_o^2}{\beta^2(\gamma-1)} \left[-\frac{1}{A} + \frac{1}{1-A} \right]_{A_{min}}^{A_{max}} \quad \ldots\ldots(8)$$

Mott or Kar and Basu :

$$\int \sigma(A) dA = \frac{2\pi r_o^2}{\beta^2(\gamma-1)} \left[-\frac{1}{A} + \frac{1}{1-A} - \log_e A + \log_e (1-A) \right]_{A_{min}}^{A_{max}} \quad \ldots\ldots(9)$$

Moller

$$\int \sigma(A) dA = \frac{2\pi r_o^2}{\beta^2(\gamma-1)} \left[-\frac{1}{A} + \frac{1}{1-A} - \log_e A \left\{ -1 \left(\frac{\gamma-1}{\gamma} \right)^2 \right\} + \log_e (1-A) \left\{ 1 - \left(\frac{\gamma-1}{\gamma} \right)^2 \right\} + \left(\frac{\gamma-1}{\gamma} \right)^2 A \right]_{A_{min}}^{A_{max}} \quad \ldots\ldots(10)$$

To obtain the total expected number of events in any knock-on energy interval, say 0.2-0.5 MEV, the results of the integrated equations 8, 9 and 10 were multiplied by the total number of electrons in 90 cm. of the emulsion that lie across the incident electron path. From the composition of Ilford G5 emulsion, as supplied by the Ilford Ltd., the number of electrons in 1 cc. of emulsion was calculated to be 1.07×10^{24}.

(*b*) *Loss correction and Results :* It appears likely that some tracks scattered sharply down into the emulsion will have been missed in the measurements. The knock-on electrons which should be uniformly distributed in Azimuth

TABLE

E_I (MEV)	E_R (MEV)	N	Theoretical estimate of no. of events		
			Rutherford (relativistic)	Mott or Kar & Basu	Möller
6.5	0.03 – 0.06	424±23	419	419	419
	0.06 – 0.10	158±13	164	164	164
	0.10 – 0.20	117±11	122	122	122
	0.20 – 0.50	71± 9	74	74	74
	0.50 – 1.00	22± 5.5	24.5	22	25
	1.00 – 2.00	10± 3.5	13	10	14
	2.00 – 3.25	6± 2.5	8	5	9
11.5	0.03 – 0.06	448±27	408	408	408
	0.06 – 0.10	187±14	162	162	162
	0.10 – 0.20	121±11	120	120	120
	0.20 – 0.50	64± 8	72	72	72
	0.50 – 1.00	27± 5.5	24	24	24
	1.00 – 2.00	13± 3.5	12.5	11	13
	2.00 – 5.75	9± 3	10	7	11
18.7	0.03 – 0.06	394±24	401	401	401
	0.06 – 0.10	145±13	160	160	160
	0.10 – 0.20	102±10.5	117	117	117
	0.20 – 0.50	63± 8	67	67	67
	0.50 – 1.00	22± 4.5	24	24	24
	1.00 – 2.00	9± 3	12.5	11	13
	2.00 – 5.00	5± 2.5	6	4.8	6.5
	5.00 – 9.35	1± 1	1.9	1.5	2.2

E_I = incident energy ; E_R = recoil energy ;
N = number of observed events, including loss correction.

about the incident direction, actually showed a marked deficiency of recoils corresponding to ejection at a large angle to the plane of the surface of the emulsion, as might have been expected from the difficulty of observation under the conditions, so that it was necessary to make a loss correction. From the departure of the distribution in Azimuthal angle from uniformity, it was estimated that this loss correction was 11%, 12% and 16.5% for incident electron energies of 6.5, 11.5 and 18.7 MEV, respectively.

The corrected numbers of recoils in the different ranges of energy are shown in the table.

(*c*) *Discussion :* Comparison of equations 8, 9 and 10 shows that, in the region of A (*i.e.* $\frac{E_R}{E_I}$) less than 0.1, the three equations are indistinguishable, the contribution from the log terms being negligibly small. In this region, the observations are seen to be in good agreement with each of the three theoretical expressions. In the region of A greater than 0.1, the three theories differ appreciably in their predictions, but unfortunately in this region the observed numbers are insufficient to make any significant comparison possible between them. In order to obtain significant differentiation, one would need to scan many times more tracks than has at present been done. This will require a great deal of scanning effort.

References

(1) Barkas et al. Phys. Rev. **86,** 59 (1952)
Phys. Rev. **88,** 1435 (1952)
(2) A. Husain, Proc. Phys : Soc. (Lond) **A. 68,** 45. (1955)
(3) C. Moller, Ann. Physik, **14,** 531 (1932)
(4) N.F. Mott, Proc. Roy. Soc. (Lond) **A 126,** 259 (1930)
(5) Kar and Basu, Ind. Jour. Phys., **18,** 223 (1946).
(6) Dilworth et al., Phil. Mag., **41,** 1032 (1950).
(7) Zajaz and Ross, Nature, **164,** 311 (1949).

PROTON-PROTON SCATTERING AT MEDIUM-HIGH ENERGIES

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Scattering experiments between nucleons constitute some of the most fundamental problems in nuclear physics and give us information about the nature of the force acting between them. In the case of proton-proton scattering, the Pauli Exclusion Principle rules out the triplet states for waves of even angular momentum (including $l = 0$) and singlet state for those of odd angular momentum. As the nuclear force is a short-range one, partial waves of $l > 2$ cannot enter the field of nuclear force, for the energy range considered here, and may thus be excluded. Even then, it has been found by recent experiments that the nuclear potential is only effective in the ^1S-state and possibly in the ^3P-state. The interference between the Coulomb and the nuclear force gives a characteristic minimum in the angular distribution and this determines the sign as well as magnitude of the nuclear phase shift which gives quantitative information on the parameters of the nuclear potential.

Breit and his collaborators[1] showed, for the first time, that the deviation of the scattering cross-section from Mott scattering is due to nuclear effects. They explained the observed discrepancy by replacing the Coulomb phase shift, σ_l, by a modified phase shift, $\sigma_l + \delta_l$, in the asymptotic solution of the Schrodinger equation for the (p-p) system. The quantity δ_l which is called the nuclear phase shift, is independent of angle and can explain the entire angular distribution at a given energy. The phase shift was related by the authors to a nuclear potential of a rectangular shape whose range and depth was $\sim 2.8 \times 10^{-13}$ cm. and ~ 10 MEV respectively. As the energy range they considered extended only upto 2.4 MEV, they considered the nuclear effect in the s-state only.

Following this pioneer work, a number of experiments were made on (p-p) scattering and more detailed knowledge of the nucleon potential was sought. Landau and Smorodinsky[8] predicted a simple functional form for the variation of the nuclear phase shift with energy under very general assumptions about the nuclear potentials. But they did not succeed in giving a rigorous mathematical derivation of the formula. Schwinger,[10] at last, related the formula to the quantum mechanical properties of the system and explained Landau and Smorodinsky's approach by a variational method. He showed that the nuclear phase shifts can be related to a set of variational parameters which, in turn, will predict the differences in the scattering properties of a short-tailed and a long-tailed well.

We shall consider here this Landau-Smorodinsky-Schwinger approach to scattering problems.[7] Under the assumptions of a short-range interaction, a certain function, K, of the nuclear phase shift and the velocity 'v' of the protons is defined as

$$K = \frac{\pi \cot \delta_o}{e^{2\pi\eta} - 1} + h(\eta) \quad \ldots\ldots\ldots \quad (1)$$

where δ_o = s-wave phase shift

$$h(\eta) = -\ln \eta - 0{\cdot}5772\ldots\ldots + \eta^2 \sum_{n=1}^{\infty} \frac{1}{n(n^2+\eta^2)}$$

and $(\eta) = \dfrac{e^2}{hv}$

The first term in the right hand side of the equation is analogous to the familiar term $k \cot \delta$ in the neutron-proton case, multiplied by the Coloumb penetration factor. The second term is due to the infinite range of the Coloumb force and is a slowly varying function of energy.

The above function, K, is related to the f-function of Breit, Condon and Present[1] and that of Bethe[3] by the relation :—

$$K = \tfrac{1}{2} f - 0{\cdot}15443$$

$$\& \quad f_{\text{Bethe}} = f + 0{\cdot}84457 \quad \ldots\ldots\ldots \quad (2)$$

Now K allows a power series expansion in the energy giving :—

$$K = R(-a^{-1} + \tfrac{1}{2} r_o k^2 - Pr^3_o k^4 + Qr^5_o k^6 - \ldots) \quad \ldots(3)$$

where R = Bohr radius of a proton bound to a fixed unit charge

and k = wave number of relative motion.

The first two co-efficients in the power series have a physical meaning. 'a' is equivalent to the Fermi scattering length,[5] evaluated at zero energy ; 'r_0' is called the effective range (of the potential well), though it is dependent both on the actual depth and the range of a particular well. If we neglect other terms in the power series, K is a linear function of energy. The two parameters 'a' and 'r_0' can thus be fitted to *any* well shape which has two adjustable constants — well depth and range. The other co-efficients (P, Q, ...etc.) of equation (3) are a measure of the deviation of the K vs. energy graph from linearity and determine the shape of the nuclear potential. It may be mentioned here that Bethe[3] has also developed a similar power series in terms of his f-function from considerations of the 'effective range theory'. One can, therefore, use either the f-function or the function K in analysing the phase shifts from proton-proton scattering data.

Application to experimental results : As has already been pointed out, experiments on (p-p) scattering below 10 MEV could hardly detect any p- or d-wave effects and experiments even upto 32 MEV produced scattering which was predominantly s-wave only.[4] Let us assume that scattering occurs in the s-state and the p-state only, upto an energy of 32 MEV and tensor forces are non-existent. Then, as the s-wave and the p-wave contributions are incoherent and the p-wave contribution is zero at 90°, a cross-section at this angle, in the centre-of-mass system, will give the s-wave phase shift exactly even if p-wave scattering is present. This phase shift will give a value of K from equation (1) and the value can be plotted against k^2 (which is a function of energy). Jackson and Blatt[7] have analysed this 90°-scattering data for values of E upto 3.5 MEV, for which region accurate values of scattering cross-section were then available. They found that all the scattering data could be related to a shape-independent formula and hence they could not discriminate between different potential well shapes. Recently Yovits et al.[11] have summarised information on low and intermediate-energy scattering. Their results show a long-tailed Yukawa or exponential potential and in the former case, the corresponding meson mass is 333 m_e.

In view of the importance of the above results in determining the shape of the nuclear potential, all the available data below 40 MEV has been collected by the author. A fresh analysis on the lines of above theory was made and the value of K obtained from each result was plotted against k^2. Table I gives all the values thus obtained :

TABLE 1.—PUBLISHED DATA ON (P-P) SCATTERING

Source	E(MEV)	k^2($\times 10^{24}$cm^{-2})	δ_a	K
RKT ..	.1675	.213	5.78±0.35	3.79±0.16
„ ..	.2002	.241	6.80±0.32	3.82±0.14
„ ..	.2259	.272	7.87±0.30	3.87±0.12
„ ..	.2495	.301	9.03±0.30	3.83±0.11
„ ..	.2753	.332	10.06±0.28	3.82±0.09
„ ..	.2983	.359	10.96±0.26	3.91±0.09
„ ..	.3214	.387	11.82±0.30	3.93±0.15
HHT ..	.670	.807	24.68±0.40	4.00±0.10
„ ..	.776	.935	27.12±0.40	4.12±0.08
„ ..	.867	1.045	29.32±0.40	4.17±0.07
HKPP ..	.860	1.036	29.28±0.40	4.15±0.03
„ ..	1.200	1.446	35.94±0.40	4.32±0.03
„ ..	1.390	1.675	38.76±0.40	4.41±0.03
„ ..	1.830	2.206	44.02±0.40	4.59±0.02

TABLE 1 (*Contd.*)

Source	E(Mev)	k^2(x10^{24}cm^{-2})	δ_a	K
HKPP ..	2.105	2.537	46.18±0.40	4.72±0.03
,, ..	2.392	2.883	48.08±0.40	4.85±0.03
BFLSW ..	2.42	2.917	48.24±0.50	4.86±0.05
,, ..	3.04	3.664	50.95±0.50	5.15±0.06
,, ..	3.27	3.941	51.89±0.50	5.24±0.06
,, ..	3.53	4.254	52.58±0.50	5.36±0.07
RWH ..	2.42	2.917	47.91±0.40	4.90±0.05
,, ..	3.04	3.664	50.80±0.30	5.17±0.05
,, ..	3.28	3.953	51.77±0.40	5.26±0.06
,, ..	3.53	4.254	52.20±0.30	5.41±0.06
MP ..	4.2	5.06	52.70±2.00	5.83±0.30
M ..	4.94±.04	5.95± .06	54.70±1.00	6.02±0.18
WC ..	8.00±.10	9.64± .12	52.70±2.00	8.00±0.40
WLRWS ..	14.5 ±.70	17.5 ±0.8	52.20±3.50	10.78±0.80
R ..	3.44	4.145	52.46±0.60	5.34±0.06
,, ..	6.85	8.254	55.82±0.60	6.86±0.12
,, ..	7.57	9.050	55.78±0.60	7.18±0.13
Mather ..	5.07	6.109	54.50±0.60	6.11±0.14
ZK ..	5.86	7.061	55.60±0.30	5.42±0.05
FW ..	12.4	14.701	53.30±0.07	9.68±0.20
AABR ..	9.7 ±.15	11.7 ± .18	57.8 ±1.20	7.68±0.20
PF ..	29.4	36.427	K is given directly in the published paper.	15.84±0.39
CJR ..	31.8	38.319	,,	16.76±0.25
Cork ..	18.8	22.654	,,	11.67±0.27
,, ..	21.9	26.390	,,	12.91±0.27
,, ..	25.2	30.366	,,	14.65±0.33
,, ..	25.45	30.667	,, ..	14.84±.27
,, ..	31.45	37.897	,, ..	16.73±.30
KKK ..	5.77	6.953	54.96±0.16	6.48±.025
WMF ..	4.2	5.061	53.80±0.08	5.69±.009
MV ..	18.3	22.052	52.8 ±0.08	11.825±.20
Hossain ..	9.5 ±.02	11.4 ±.02	53.9 ±1.5	8.56±.24
CH ..	9.7 ±.05	11.6 ±.05	56.5 ±0.10	7.94±.10
YW ..	18.3 ±.24	21.8 ±.24	53.2 ±0.90	11.40±.20

References for the abbreviations in Table I

1. RKT — To be found in the Table given by Jackson and Blatt.
2. HHT — To be found in the Table given by Jackson and Blatt.
3. HKPP — To be found in the Table given by Jackson and Blatt.
4. BFLSW — To be found in the Table given by Jackson and Blatt.
5. RWH — To be found in the Table given by Jackson and Blatt.
6. MP — To be found in the Table given by Jackson and Blatt.
7. M — To be found in the Table given by Jackson and Blatt.
8. WC — To be found in the Table given by Jackson and Blatt.
9. WLRWS — To be found in the Table given by Jackson and Blatt.
10. R — Rouvina, Phys. Rev., **81,** 593 (1951).
11. Mather — Mather, Phys. Rev., **82,** 133 (1951).
12. ZK — Zimmerman and Kruger, Phys. Rev., **83,** 218A (1951).
13. FW — Faris and Wright, Phys. Rev., **79,** 577 (1950).
14. AABR — Allred, Armstrong, Bondelid and Rosen, Phys. Rev., **88,** 423 (1952).
15. CJR — Cook, Johnston and Richman, Phys. Rev., **79,** 71 (1950).
16. C — Cork, Phys. Rev., **80,** 321 (1950).
17. KKK — Kerman, Kreger and Kruger, Phys. Rev., **89,** 908A (1953).
18. WMF — Worthington, McGruer and Findley, Phys. Rev., **90,** 899 (1953).
19. MV — Martin and Verlet, Phys. Rev., **89,** 519 (1953).
20. Hossain — Hossain, Ph.D. Thesis, University of Bristol (1955).
21. CH — Cork and Hartsough, Phys. Rev., **94,** 1300 (1954).
22. YH — Yntema and White, Phys. Rev., **95,** 1226 (1954).

A least square method was used to obtain the best value of the parameters, a, r_0, P, in equation (3). The equation found for the best fit is

$$K = 3.6856 + 0.4158(5)k^2 - 0.001942k^4 \ldots\ldots (4)$$

This gives:

$$a = -7.818 \times 10^{-13} \text{ cm.}$$
$$r_0 = 2.886 \times 10^{-13} \text{ cm.}$$
$$P = +0.028$$

Figures 1 and 2 show that while the line of best fit is indistinguishable from a straight line upto an energy of about 5 MEV, appreciable departure from P =0 line is indicated by the same curve beyond 5 MEV. The value of P clearly indicates that the effective potential is a long-tailed one and the potential well falls between the exponential and the Yukawa type. If we assume a Yukawa well, which is the only one with a theoretical basis, the corresponding meson mass is 318 m_e. This is in agreement with the value obtained by Breit and Hatcher[2] when they express their f-function as a quadratic series in E, but is lower than the masses obtained by Yovits et al.[11] and Hoisington et al.[6] The difference of mass between this Yukawa particle and π-meson, whose mass is 273 m_e, is much more than any relativistic correction, or a correction due to a cut-off in the meson potential. Breit and Hatcher,[2]

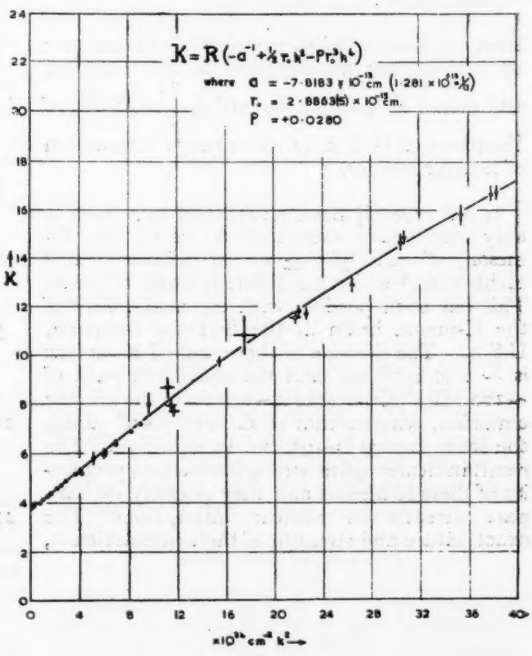

Fig. 1.

Experimental values of K plotted vs. k2 for all published data on (p-p) scattering below 40 MEV. The least square fit to these experimental points is also given, showing that the best curve is quadratic.

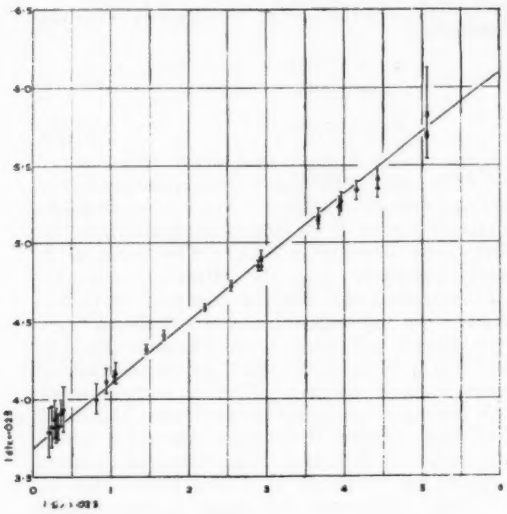

Fig. 2

A detailed and magnified plot of the experimental points at energies 5 MEV, with the least square line of figure 1. It is seen that for such low energies, the curve is partically indistinguishable from a straight line.

however, have tried to explain this discrepancy by introducing a correction to the Coloumb and meson term in the potential, $\frac{\epsilon_2}{r} - \frac{C_e - \gamma/_a}{\gamma/_a}$, of Yovits et al.[11] due to short-range interaction of heavier mesons.

It has recently been established that there is only one heavy meson (now called the K-meson) of mass 965 ± 10 m_e (Ritson et al.,[9] Hebb et al.,[6]) which has different modes of decay. This has been possible with the availability of the K-meson beam at the Berkeley Bevatron, U.S.A. The lifetime of these unified K-mesons is $\sim 1 \times 10^{-8}$ sec. and the mean free path of ~100 MEV K-mesons is ~25 cm. in the nuclear emulsion, whereas that of K^+-mesons of about the same energy is ~95 cm. in emulsion. The result indicates quite strong interaction properties of these K-mesons and they possibly do take part directly in nuclear interactions. The exact nature and strength of their interaction is, however, still uncertain. It is therefore understandable that the meson mass obtained in proton-proton experiments (assuming Yukawa potential) will be larger than the π-meson, as it is the effective mass due to contributions from both π- & K-mesons.

References

1. Breit, Condon and Present, Phys. Rev., **50,** 825 (1936).

   Breit, Thaxton and Eisenbud, Phys. Rev., **55,** 1018 (1939).

2. Breit and Hatcher, Phys. Rev., **78,** 110 (1950).

   Breit and Hatcher, Phys. Rev., **87,** 375 (1952).

3. Bethe, Phys. Rev., **76,** 38 (1949).

4. Cork, Phys. Rev., **80,** 321 (1950).

5. Fermi and Marshall, Phys. Rev., **71,** 661 (1947).

6. Hebb, Chupp, Goldhaber and Goldhaber, Phys. Rev., **101,** 1212 (1956).

   Hoisington, Share and Breit, Phys. Rev., **56,** 884 (1939).

7. Jakcson and Blatt, Rev. Mod. Phys., **22,** 77 (1950).

8. Landau and Smorodinsky, J. Phys. U.S.S.R., **8,** 154 (1944)

9. Ritson, Pevsner, Fung, Widgoff, Zorn, Goldhaber and Goldhaber, Phys. Rev., **101,** 1085(1956).

10. Schwinger, Phys. Rev., **72,** 742A (1947); hectographed notes on Nuclear Physics, Harvard (1947).

11. Yovits, Smith, Hull, Bongston and Breit, Phys. Rev., **85,** 540 (1952).

DESIGN AND STUDY OF AUDIO- AMPLIFIER AND RADIO-RECEIVER USING TRANSISTORS

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TRANSISTORS are nowadays being used more and more in hearing aids, radio and television receivers and other tele-communication equipment. Being of recent origin the transistors are constantly being improved by the manufacturers. Alongside of this, there is ample scope for improving the performance of existing units through better circuit designs.

Many circuit designs of transistor amplifiers and receivers are available in the current literature, in most of which interstage transformer coupling has been used. However, in hearing-aid circuits, resistance-capacity coupling has found favour due to compactness and light weight. Power handling capacity of hearing aid transistors is small and so even for hearing aid amplifiers a number of transistors have to be used. The successful use of transistors in hearing aid encouraged us to build low cost and light weight audio-amplifiers of different designs and to study their performance characteristics. Three different types of amplifiers using three hearing-aid type transistors (number OC70/OC71) in each were built. For each of the three amplifiers, the relative voltage gain at different frequencies and also at different input levels was measured. Moreover, the harmonic distortion in all the three amplifiers was studied.

Finally a semi-conductor diode was incorporated in one of the amplifiers to convert it into a radio receiver.

Design

In using a transistor in place of a radio valve either the base or the collector or the emitter may be earthed. Each method has its advantages and disadvantages. For example, when an amplifier is built in the earthed emitter to earth-emitter arrangement, it has a high gain, but its distortion figure is also correspondingly high. For low distortion, an earthed base arrangement is suitable.

Our aim was to use hearing aid transistors giving the high voltage gain needed for a radio receiver. So in our design, the earthed emitter arrangement was preferred. Our next step was to find out a suitable cascading arrangement which would give low distortion.

Now the input and output impedances are given by the following equations :

$$R_{in} = r_{11} - \frac{r_{12}r_{21}}{r_{22}+R_L} \quad \ldots\ldots\ldots\ldots (1)$$

$$\text{and, } R_{out} = r_{22} - \frac{r_{12}r_{21}}{r_{11}+R_S} \quad \ldots\ldots\ldots\ldots (2)$$

where r_{11} = incremental emitter resistance for an incrementally open-circuited collector.

r_{12} = incremental backward transfer resistance for an incrementally open-circuited emitter.

r_{21} = incremental forward transfer resistance for an incrementally open-circuited collector.

r_{22} = incremental collector resistance for an incrementally open-circuited emitter.

R_L = load resistance.

R_S = resistance of the signal source.

The presence of the load impedance term R_L in (1) and the source impedance term R_S in (2) indicates that there is much more interaction between the input and the output than there is in a valve. Thus cascading transistors need rather a careful arrangement.

In our design the values of resistors R_1, R_2, R_3 and R_4 (fig. 1) for stability of the circuits were determined empirically. The potential divider controls the base bias, R_4 is used for stabilising negative feed back, and R_3 is the load resistance. All the components were of standard sizes used in valve circuits.

Gain and Distortion

Schematic diagram of the experimental set up for the measurement of gain is shown in figure (2). For the distortion measurement, the output meter was replaced by the distortion analyser.

The output of the signal generator was connected to a potentiometer which in turn

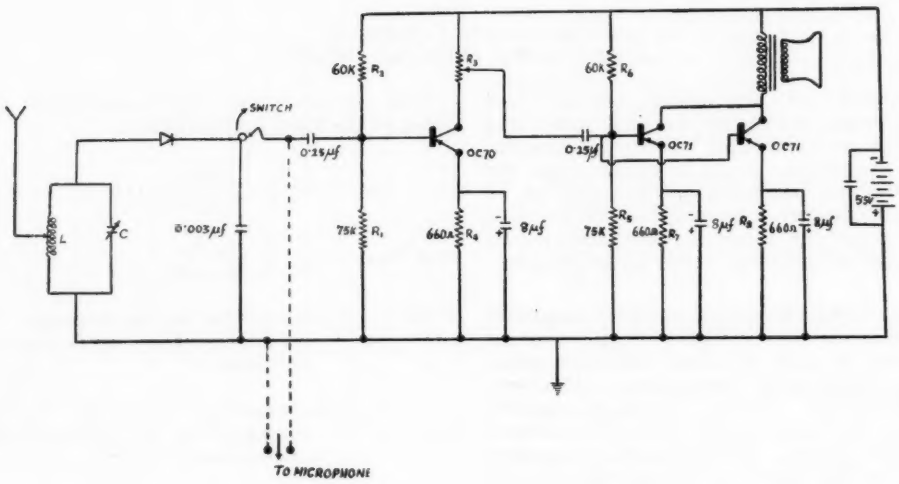

Fig. 1.—Circuit diagram of a transistor receiver.

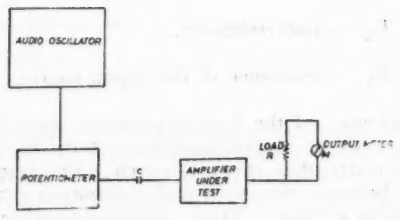

Fig. 2.—Schematic diagram of apparatus for measuring circuit gain.

was coupled to the amplifier input by means of a coupling condenser C. The amplified output voltage was developed across the load R. An output meter (M) was connected across the load. Two series of measurements were made. In the first case the frequency of the signal was kept constant while the amplitude was varied and in the second case the amplitude of the signal was kept constant while the frequency was varied. The gain of the amplifier is given by the formula :

$$N_{db} = 20 \log V_2/V_1 + 10 \log Z_1/Z_2 + 10 \log K_2/K_1$$

where subscript 1 refers to input and 2 refers to the output. V, Z, K denote voltage, impedance and power factors respectively. It should be noted that for a resistive load the last term vanishes. When the input and output resistances are equal, the second term also vanishes. If, however, they are not equal, $20 \log V_2/V_1$ shows the nature of the gain curve but does not give its value.

In measuring distortion both type TF455D/1 Wave Analyser of Marconi and Model 330B distortion analyser of Hewlett-Packard were used. The signal source was Model 206A Audio Oscillator of Hewlett and Packard. The experimental arrangement was similar to that in the previous case except that in place of the output meter the distortion analyser or Marconi Wave analyser was used. The distortion analyser measured the percentage of total distortion while the wave analyser measured the percentage of distortion due to any of the harmonics. As in the case of gain measurements, the distortion was measured for different amplitudes of the signal at a constant frequency and for different frequencies at a constant input signal level.

Some of the experimental results are shown graphically, (figs. 3-6).

The present investigation has shown that hearing aid transistors can deliver enough

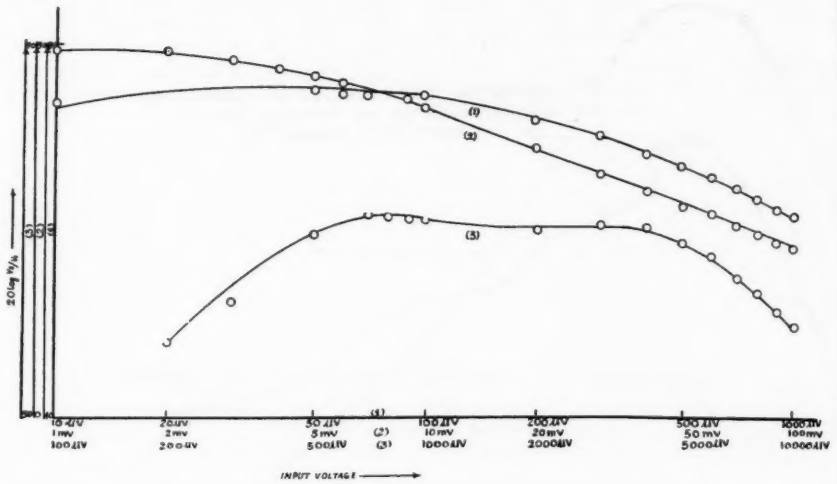

Fig. 3.

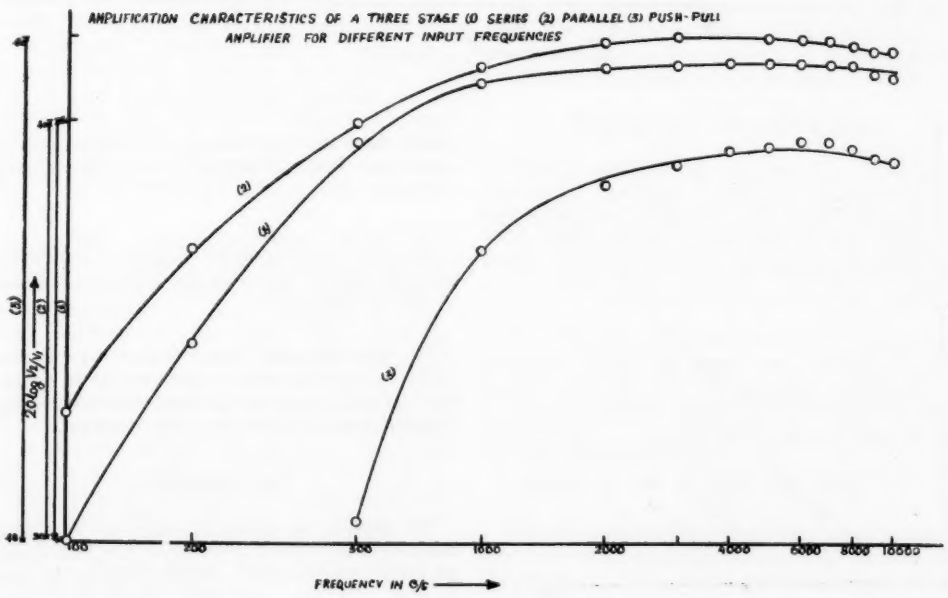
AMPLIFICATION CHARACTERISTICS OF A THREE STAGE (1) SERIES (2) PARALLEL (3) PUSH-PULL
AMPLIFIER FOR DIFFERENT INPUT FREQUENCIES
FREQUENCY IN C/S

Fig. 4.

power even when R-C coupling is used. These transistors were found to be most suitable for low level amplifications. Cascading of more than two of them in series lowered the overall voltage gain and increased distortion when the input signal was as high as 10 mV. At 1 mV input the overall amplification for three stage series, parallel or push-pull amplifiers were

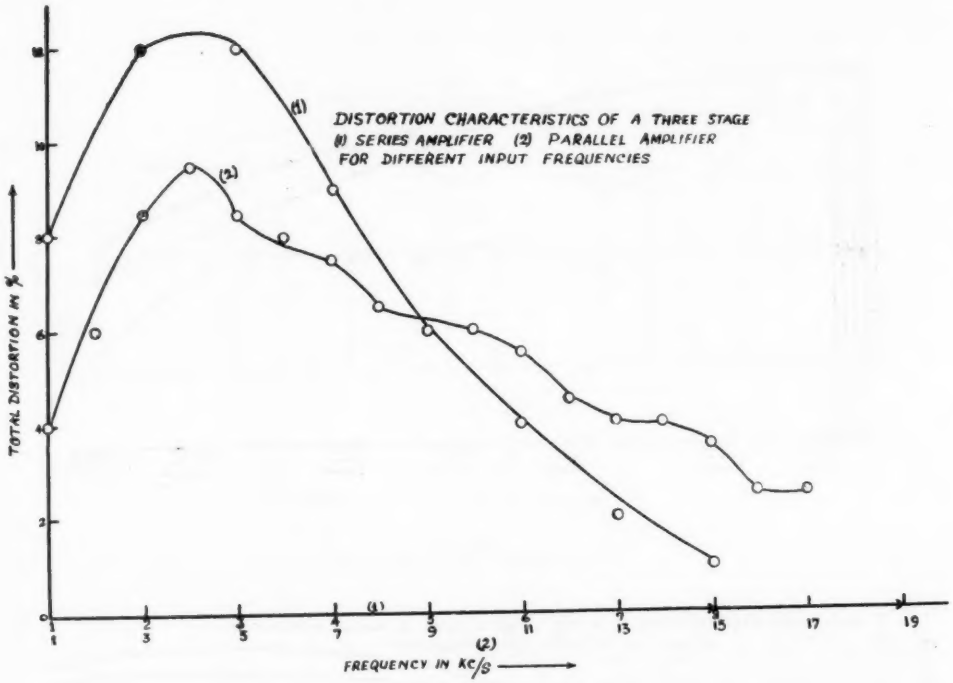

Fig. 5.

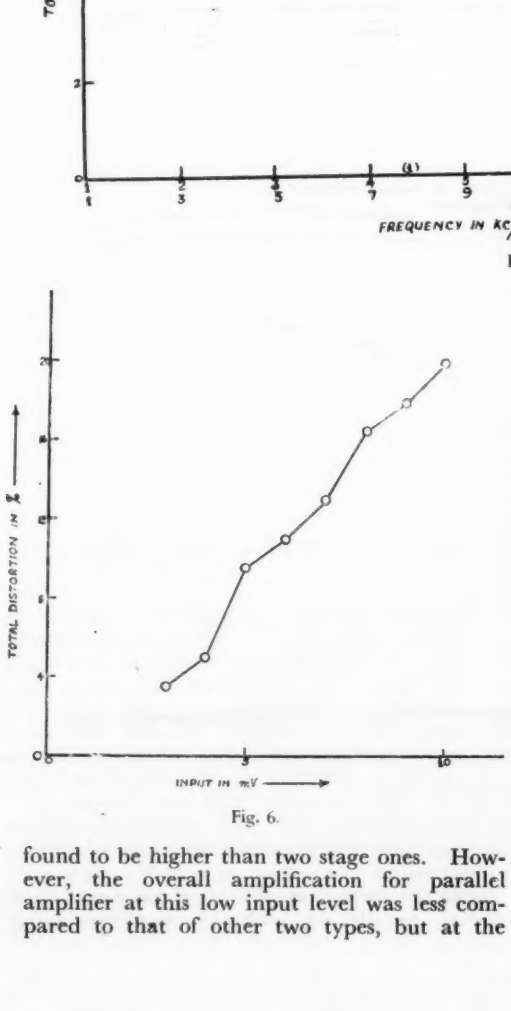

Fig. 6.

found to be higher than two stage ones. However, the overall amplification for parallel amplifier at this low input level was less compared to that of other two types, but at the same time the percentage of distortion in this case was lower compared to other arrangements.

At 0.03 mV input the voltage amplification was as high as 5,000 in the case of three-stage series arrangement.

The amplification was found to increase with increasing supply voltage till it reached the value of 5.5 volts. beyond which the amplification remained more or less constant.

The Receiver

By adding a detector stage to any audio amplifier, it is possible to convert it into a radio receiver provided the rectified signal is strong enough for the amplifier. Since our transistors were of the low level type, the amplifier was suitable for such conversion. Because of low distortion and fewer component requirement the parallel amplifier was selected. A germanium crystal diode with a tuning circuit was added to the amplifier and it was converted into a good local receiver.

At a distance of about 20 miles from the local radio station the programme was very clearly heard with good loudspeaker strength using an improvised antenna. At night the programme from Calcutta and even Ceylon could be heard in loudspeaker strength, but the fading was severe.

The power consumption was only 5 ma at 6 volts. Thus four flash-light cells would supply enough power to operate the receiver for several hundred hours.

Since resistance-capacity coupling was used throughout, the initial cost of the receiver was also comparatively low.

DESIGN OF AN IMPROVED TYPE OF DRY CELL

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THE dry Leclanche cell, which has proved itself to be a most convenient and fully proved source of portable power, is today one of the major callers on the world zinc supplies, because of its variety of uses, which include portable telecommunication equipment, hearing aid appliances, portable wireless receivers, and transisterized electronic equipment. In the usual type of dry-cell, only a small fraction of the zinc forming the outer vessel is utilized chemically. It is, therefore, of considerable importance to investigate methods for a more economic utilization of the zinc in such cells.

The present investigation aims at (a) improving the quality of the dry-cell by giving it longer life and (b) incorporating the minimum possible quantity of zinc compatible with proper working of the cell. The essential feature of our new design is that the zinc is in the form of a fin-shaped rod and constitutes the inner electrode instead of the outer one as in the usual type of dry-cell. Two cells using the same quantities of the chemicals in identical proportions were prepared, one according to the usual pattern and the other according to our improved design. These two cells were discharged under identical conditions of test so that a comparative study of their performances was made.

The investigation was restricted to a measurement of the relative power output of the two cells. Due to the non-availability of the proper quality of the chemical ingredients, an exhaustive study of the improved cells could not be made, neither was a direct comparison of these cells possible with the commercially manufactured cells. Nevertheless, the superiority of the improved type of cells over the conventional design appears to be proved by our comparative methods of test. It is hoped that the present communication will induce manufacturers in our country to make a break with tradition and try out the new type of cell.

Theoretical Considerations

The Leclanche cell produces a current of electricity by the chemical consumption of zinc, the flow of electricity through the external load circuit being maintained by the chemical energy liberated in the following reaction :

$$2NH_4Cl + Zn = Zn\,Cl_2 + 2NH_3 + 2H$$

To counteract the polarization caused by the liberated hydrogen, manganese dioxide is used as the de-polariser. Its action, which occurs in the immediate vicinity of the carbon electrode, can be represented approximately by the following equation :

$$_2MnO_2 + 2H = Mn_2O_3 + H_2O$$

The de-polarization, however, soon becomes less effective, perhaps because of the actual chemical reaction being more complex than indicated by the above equation. Therefore, the effectiveness and the voltage of the cell drops sharply if it is used continuously for extended periods.

Assuming that the zinc is used with 100% efficiency, it is easy to calculate how many ampere hours will be produced by an average

cell, whose zinc container weighs approximately 19 g. Since one g. equivalent (*i.e.*, 32.7 g.) of zinc if consumed will produce one faraday of electricity *i.e.*, 96,450 coulombs, it follows that 19 g. of zinc would produce $96{,}450 \times \frac{19}{32.7} = 56{,}000$ coulombs, *i.e.*, $\frac{56{,}000}{60 \times 60} = 15.6$ ampere hours. Thus, if the zinc is completely consumed, our cell should give 15.6 ampere hours as against the normal rating of about three ampere hours. It follows that only about 20% of the zinc is usefully consumed, the major part going waste.

Constructional Details

Figure 1 shows the constructional details of a conventional type of dry-cell. The carbon rod together with the de-polarizing paste are to be considered as a composite electrode, the de-polarizing action taking place at the outer surface of the paste and proceeding inwards as the cell is progressively discharged. Between the de-polarizing paste and the zinc container is the electrolytic paste. The electrolyte is made up of ammonium chloride, zinc chloride, starch, and plaster of Paris, with enough water to make a paste. The de-polarizing mixture is usually made up of MnO_2 and graphite together with a small proportion of the electrolyte. The exact compositions are, of course, a trade secret.

Some suitable methods must be adopted to prevent the carbon rod and the de-polarizing paste from touching the bottom of the zinc container, otherwise a short-circuit results; this separation is usually accomplished by putting an insulating material such as cardboard, soaked in paraffin wax (seen at E in figure 1) in the bottom of the zinc can. The dimensions of a medium (torch) dry cell are as below :

Length of the prepared zinc can ..	$2\frac{1}{4}$ in.
Diameter of the can	$1\frac{1}{4}$ in.
Weight of the zinc used in the can	19 g.
Weight of depolarizing mixture ..	46 g.
Weight of electrolytic paste ..	10.25 g.

The modified dry-cell proposed by the authors is essentially a sort of inverted cell (fig. 2) with the zinc electrode in the middle and the carbon electrode on the outside of the cell. The zinc electrode is fin-shaped as shown in figure 3. The outer carbon electrode is prepared by taking a hollow glass-tube, with a small hole at the bottom, into which fits a binding terminal of copper, and depositing graphite powder on the inner surface of the tube. The deposition was done by making the graphite powder in the form of a suitable paste by adding a little sticky substance to it. The paste was then spread uniformly over the inner surface of the tube and then allowed to dry up. This method is defective because it increases the internal resistance of the cell due to non-compactness of the graphite particles. The internal resistance of the cell could be reduced considerably if the outer carbon (graphite) electrode could be made by hydraulic pressure, so that the carbon granules would be much more compact. But unfortunately no such press was available in our laboratory.

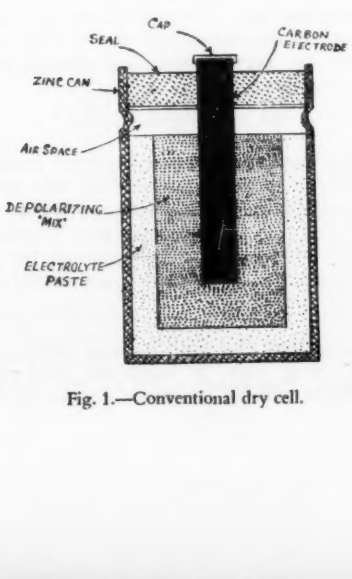

Fig. 1.—Conventional dry cell.

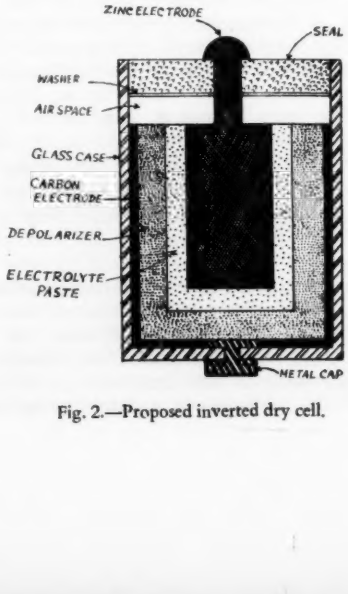

Fig. 2.—Proposed inverted dry cell.

Fig. 3.—Zinc electrode in proposed cell.

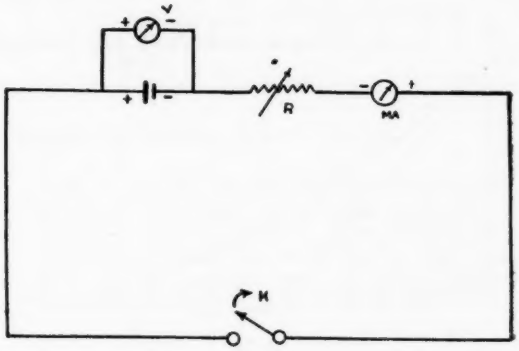

Fig. 4.—Discharge circuit.

Having prepared the carbon electrode, the depolarizing mix was placed inside it and pressed sufficiently, keeping a gap for introducing the electrolytic paste which surrounded the fin-shaped zinc electrode. The electrolytic paste with the zinc electrode was then placed in the gap. Any residual space left was filled in by pouring the electrolytic paste in it and then allowing the paste to set. The rest was done as in the previous case. The preparation of the depolarising mix and the electrolytic paste was also similar to the previous case. The exact arrangement is shown in figure 2.

Dimensional and other data are given below :—

Weight of the fin-shaped zinc electrode	19 g.
Diameter of the fin-shaped zinc electrode	$\frac{3}{4}$ in.
Length of the fin-shaped zinc electrode	2 in.
Weight of the depolarising mix ..	46 g.
Weight of the electrolytic paste ..	10.25 g.
Length of the glass tube ..	$2\frac{1}{2}$ in.
Inner diameter of the glass tube ..	$1\frac{1}{4}$ in.

The two cells thus prepared were then put under experimental test.

Testing Procedure

The two cells were connected to two separate but similar circuits and were allowed to discharge through a resistance (fig. 4). The two cells were subjected to continuous discharge. In the discharge process the current was kept constant by varying the ohmite rheostat R and the fall of voltage with time was noted. The cells were discharged till they attained a closed-circuit voltage of value 0.10 volt. The total ampere hour obtained for each individual case was then calculated.

The usual way of discharging a cell is by an intermittent process *i.e.*, to discharge the cell for a convenient period, then to stop discharging and again to start the process. But we discharged the cell continuously *i.e.*, under the most unfavourable condition with a view to establishing the fact that performance will definitely be better under the intermittent process than under the continuous process of discharging.

It is to be noted that in the case of both the conventional cell and the improved type of cell the internal resistance was high because they were hand-made. If suitable high-pressure machines were used the internal resistance could be made very small. Due to the large internal resistance the discharge rate was kept very low. The results of the discharge are shown graphically (fig. 5).

Discussion of Results

The conventional cell was continuously discharged for 163 hours at 15 ma constant current during which period the open circuit voltage dropped from 1.7V to 0.7V. Thus 2.445 ampere hour was taken out.

The modified cell was continuously discharged for 288 hours at 15 ma constant current

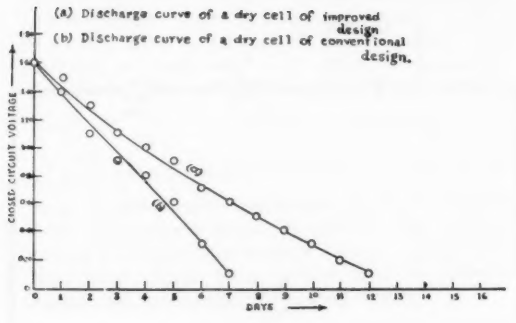
(a) Discharge curve of a dry cell of improved design
(b) Discharge curve of a dry cell of conventional design.
CLOSED CIRCUIT VOLTAGE
DAYS

Fig. 5.

during which period the voltage dropped from 1.7V to 0.7V. In this case 4.32 amp. hours of energy were taken out. Thus the modified cell was found to be 43.4% more efficient than the conventional one.

The improvement in the capacity of the cell was due entirely to the design and arrangement of the electrodes. However, both the cells constructed in the laboratory suffered from the defect of high internal resistance. Resistance of the carbon electrode depends primarily on the compactness of the carbon granules forming it. For want of any press it was not possible for us to prepare a compact cylindrical carbon container required for the construction of the cell of improved design.

Moreover, MnO_2 used by us contained iron as an impurity. This caused local action and as such the efficiency was reduced.

Inspite of these defects the cell designed non-conventionally exhibited higher efficiency due primarily to two factors :

(1) The area of the carbon electrode surface exposed for the depolarisation was higher ; and

(2) the zinc was more completely used up. In the case of a conventional cell, when the zinc container is perforated, it becomes useless, whereas, in the case of our improved design, the question of perforation does not arise. This ensures longer life and hence higher capacity.

Thus it may be concluded that for the same amount of material much higher efficiency is obtainable if the cells are designed along the lines suggested above.

STUDIES IN THE PROPERTIES OF HEAT INSULATING BUILDING MATERIALS

Part 1.—Mixtures of Cement and Rice-Husk Ash

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THE flow of heat across the walls, roofs, and other partitions in a building is a factor of considerable importance in the design of houses, and other structures, in order to maintain a comfortable temperature with a minimum of expense. This is particularly so in case of factories and offices, where the temperature should be kept within definite limits to obtain maximum efficiency from the workers. For all such temperature control, the thermal properties of the building materials used are of prime importance. A study has therefore been carried out to evolve suitable compositions for building materials from locally available resources with particular reference to thermal insulation and mechanical strength.

Rice-husk is available in large quantities in the rice growing belts of Pakistan, and is at present mostly used as fuel in the rice husking industry. Occasional attempts have been made to utilize it as a component in the production of certain building materials. In Pakistan, for example, Messrs Gammon (Pak), Ltd., have used blocks made of cement and rice husk under the name "Feather-crete" for insulating the shell construction roofs at Fauji Textile Mills, Jhelum. These blocks were made in $2' \times 2' \times 1''$ size, using a 3:1 ratio by weight of cement and rice husk, the mixing water containing 4% sodium silicate. The thermal conductivity of this type of block was determined in the Building and Road Research Laboratory, Punjab P.W.D., Lahore, and was found to be 0.13×10^{-3} c.g.s. unit. A disc of 10.0 cm. diameter, 2.5 cm. thick, made to the same specifications, was also tested in the Central Laboratory for its thermal conductivity, and a value of 0.15×10^{-3} was obtained, as against the tabulated values, 0.11×10^{-3} for cork, and 0.5×10^{-3} for wood, which goes to show that the incorporation of rice husk imparts very good insulating properties to cement blocks. However, the structural strength of the cement-rice-husk blocks is low and, therefore, they cannot be designed to take any appreciable stress. There is also the danger of organic decay of the rice husk.

It was felt that a possible way out of these difficulties might be the substitution of rice-husk by the ash left after burning the material as a fuel, on account of the tough and cellular structure of its particles. This idea found a certain measure of support in the fact that rice-husk ash has actually been successfully incorporated in the production of clay bricks.[1]

Measurement of Conductivity

In order to explore this possibility a systematic study has been made of the performance of cement and rice husk ash blocks of various compositions extending from 5:1 upto 1:20 of the two components by volume. For the measurement of thermal conductivity, the samples were made as discs 10 cms. in diameter and 2.5 cms. thick. The coefficient of thermal conductivity of such a disc can be measured by using Lee's disc method (fig. (1)), wherein the sample (in the form of a disc of area 'A' and thickness 'd') is placed between a cylindrical steam chest and a metal disc freely suspended in the atmosphere. The equilibrium temperature, θ_E, of the disc has been obtained by a new method developed in these laboratories, namely by plotting $\delta\theta/\delta t$ against θ and extrapolating to $\delta\theta/\delta t = 0$. This technique has the advantage of considerably saving time. The coefficient of thermal conductivity is calculated by means of the formula :—

$$K = \frac{d}{A} \times \frac{\theta_E - \theta \text{ ambient}}{\theta \text{ steam} - \theta_E} \times E(A + A'),$$

where A = area of cross-section of disc, A′ = area of cylindrical surface of metal disc, E = its emissivity.

The emissivity is obtained by measuring the free cooling curve of the disc and calculating

$$\frac{\delta\theta}{\delta t}/(\theta - \theta \text{ ambient}),$$

$$\text{whence } E = \frac{m\,s}{2A + A'} \left\{ \frac{\delta\theta}{\delta t}/(\theta - \theta \text{ ambient}) \right\}$$

where m = mass of the metal disc,

s = specific heat of the metal.

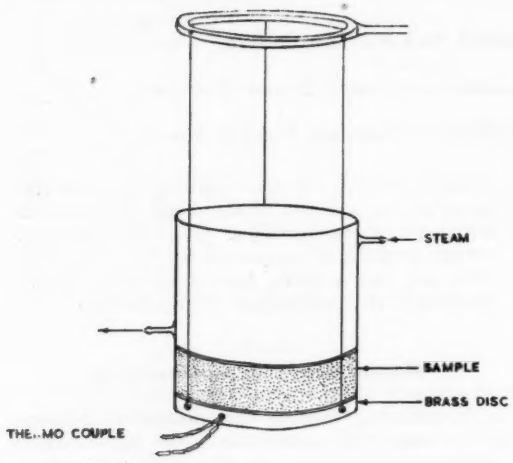

Fig. 1 (a).

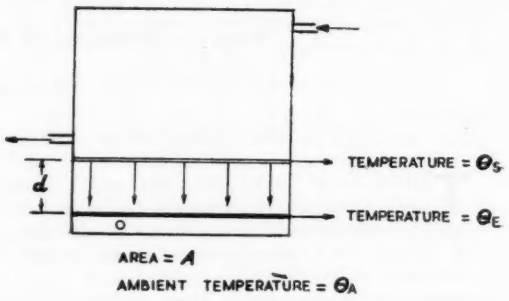

Fig. 1 (b).

A simple way of obtaining the correction to be applied for the heat lost from the exposed cylindrical surface of the sample has been worked out, which consists in repeating the measurement with a sample of twice the thickness. If K_1 and K_2 are the two measured values of K, the correct value of K is given by $K_{corr.}=K_1+1/2\ (K_1-K_2)$ to a good approximation. The detailed theory and experimental verification of this will be given in a separate communication.

Results Obtained

The experimental results of the thermal conductivity measurements on the discs of cement rice husk ash are shown in table (1) together with the measured densities and tensile strengths of the discs. The densities were obtained by weighing the disc and calculating its volume from its dimensions. In the table, K is the heat in gram calories transmitted per sq. cm. of cross-section per unit thickness (cm.) per second for each 1 °C. difference of temperature. The estimated error of the experimental values is $\pm$ 0.02×10-3. The tensile tests were carried out on special briquettes of one inch square effective cross-section made in accordance with British Standard Specifications No. 12/1947, the samples being tested after curing for seven days.

In table (2) are given for comparison the thermal conductivities of a few of the commoner building materials, of which Nos. 1 and 2 have been measured in this laboratory.

Discussion of Results

As was to be expected from the cellular structure of the rice husk ash, the thermal conductivity of the samples containing large quantities of this ash is very low, the value for the ash being about 0.15×10^{-3}. This last value was obtained by filling a Petri dish with the ash, levelling the free surface with a glass plate, and then measuring the K-value of this composite sample and correcting the result for the effect of the glass bottom of the dish. (Since the loose ash is very compact, the result will not be very different even if the ash is packed in the dish under considerable pressure.) This value is about twice that for air. However, the introduction of large quantities of ash in the sample results in a very marked lowering of the tensile strength, so that a compromise is to be sought at some intermediate composition. The measurements of table (1) are shown graphically in the three curves of figure (2). The curves for tensile strength and density show a monotonous decrease with increasing ash content according to expectation, whereas the graph for the thermal conductivity shows an anomalous behaviour insofar as it has an intermediate minimum followed by a maximum. The density curve seems to be made up of two straight lines, separated by a rather sharp bend at approximately 90% by volume of rice husk ash. This suggests that, in certain ranges of composition, there is perhaps a special interaction between the three components *viz.*, cement, water, and rice husk

TABLE 1

Sample No.	Proportions cement : rice husk ash by vol.	Vol. % of rice husk ash	Measured density g./c.c.	Wt. % of rice husk ash	$K \times 10^{-3}$	Tensile strength lbs/in^2.
1.	1:0	0.0	2.00	0.0	0.68	375
2.	5:1	16.7	1.93	2.0	0.53	320
3.	2:1	33.3	1.73	5.0	0.47	290
4.	1:1	50.0	1.53	10.0	0.42	250
5.	1:2	66.7	1.32	17.0	0.47	185
6.	1:3	75.0	1.35	23.1	0.50	190
7.	1:4	80.0	1.25	28.6	0.49	160
8.	1:5	83.3	1.20	30.3	0.43	150
9.	1:6	85.7	1.07	37.4	0.41	140
10.	1:8	88.9	1.08	44.4	0.42	80
11.	1:10	90.9	0.87	50.0	0.36	—
12.	1:15	93.8	0.67	60.0	0.27	~0
13.	1:20	95.2	0.68	66.6	0.26	
14.	0:1	100.0	0.20	100.0	0.15	

TABLE 2

Serial No.	Material	K-Value as determined in the Laboratory ($\times 10^{-3}$)	K-Value, as obtained from the literature ($\times 10^{-3}$)
1.	Cement : ordinary sand (1:3 by wt.) 12.5% water	0.77 ± 0.03	
2.	Cement (local)	0.68 ± 0.03	
3.	Wood	- - -	0.5
4.	Cork	- - -	0.11
5.	Cotton wool	- - -	0.06
6.	Air (still and dry)	- - -	0.06

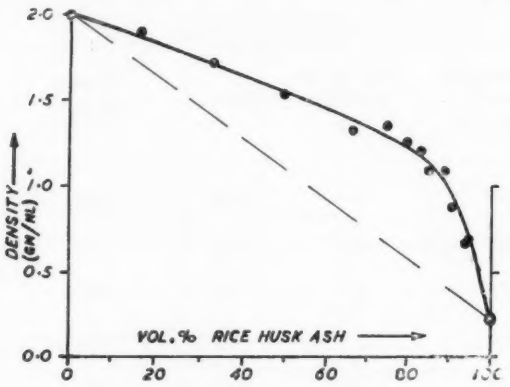

Fig. 2 (a).

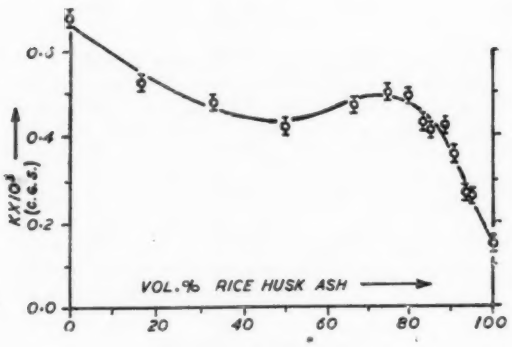

Fig. 2 (b).

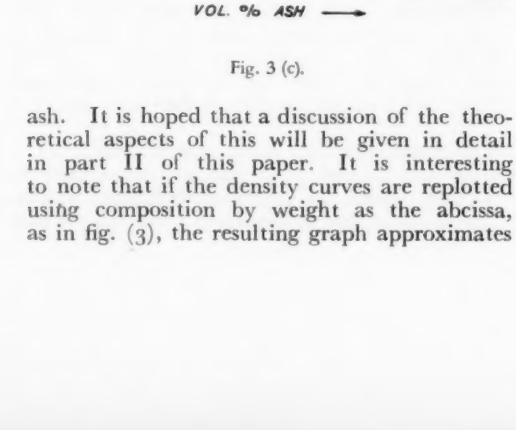

Fig. 3 (c).

ash. It is hoped that a discussion of the theoretical aspects of this will be given in detail in part II of this paper. It is interesting to note that if the density curves are replotted using composition by weight as the abcissa, as in fig. (3), the resulting graph approximates

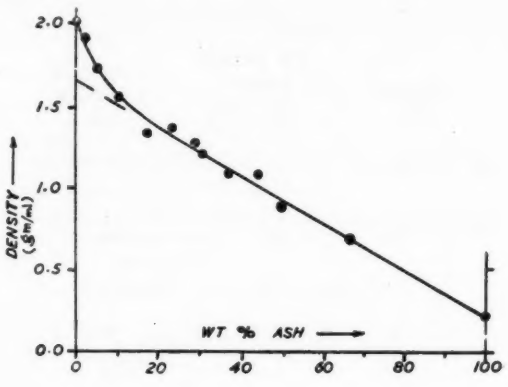

Fig. 3.

to a straight line, except for the initial part, which lies somewhat above the extrapolation of this straight line.

The curve for thermal conductivity is particularly interesting in that there exists a minimum at about 50% by volume of ash. The importance of this lies in the fact that this composition of rice husk ash and cement has a good tensile strength value of 250 lbs. per square inch (cf. about 300 lbs/ sq. inch for cement concrete), while the K-value is 0.42×10^{-3}, or 60% of the value for cement and cement concrete. This is particularly significant because we can thus obtain a material with a strength comparable with cement concrete and about twice its heat insulation. The cost also will not be materially affected, because the rice husk ash required is about 50% by volume amounting to only 10% by weight. The cement consumption can be further cut down by using mixtures of cement, sand, and rice husk ash in suitable proportions, which are being worked out in these laboratories. Such a material could be used with advantage as a surface plaster in hotter climates and even as a structural material in place of cement concrete.

If a material of very low conductivity is needed (*e.g.*, for air conditioning, etc.) it will be necessary to use rather high percentages of rice husk ash, around 60% by weight for $K = 0.2 \times 10^{-3}$. Apart from the economic unfeasibility of this, there is the added disadvantage that such a composition has a very low tensile strength, cf. figure 2(c), which would limit its use to non-weight bearing structures like partition walls.

Thus it is seen that the anomalous behaviour shown by the thermal conductivity curve for various compositions of cement and rice husk ash furnishes a building material of considerable practical utility, with the added advantage of a high resistance to fire and insect attack. The theoretical explanation of the anomalous minima and maxima in the thermal conductivity curves involves detailed discussion of the structure of the constituents and their interaction during setting, which will form the subject matter of Part II of the present paper.

Acknowledgements

Grateful acknowledgement is made to Mr. H.T. Bellamy, I.C.A. Ceramic Expert, for the reference to News Review and for helpful discussions.

Reference

1. News Review, 1956, Vol. VII, No. 15, page 7, published by the United States Information Services.

PRELIMINARY EXAMINATION OF CLIFTON SAND

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WHEN rocks and minerals are broken down, either by natural or artificial agencies, the products are classified as gravels, sands, silts, and clays, the term sand being usually applied to the material of diameter between about 1/20 mm. and 2 mm. In certain shore and river sands, the heavier rock-forming minerals like garnet, tourmaline, rutile, pyroxenes, iron ore, etc., get concentrated as a result of current action, and economically valuable deposits may then be obtained. The black and lustrous coastal sand from Clifton beach seems to be of the latter kind. As a result of preliminary investigations carried out at the Central Laboratories, it was found that nearly 50% of this sand is acid soluble and the insoluble portion is micaceous in appearance, as against the usual run of sands, which consist of about 90% silica. In view of the high mica content of the sand and its large acid soluble fraction, which might prove a significant source of rare elements, a detailed chemical investigation of the Clifton beach sand has been undertaken. The present paper deals with the results of the analysis and the concentration of certain constituents of these sands.

The coastal sand from Keamari to Korangi, a stretch of about 10 miles, is black in appearance, but on close examination it was found to contain black and white lustrous platy particles in addition to calcareous and siliceous material.

The acid soluble fraction contains a large proportion of iron (about 20%) beside an average of about 3% of aluminium, 5% of magnesium, and 1½% of titanium. The sand, moreover, shows a marked degree of radioactivity, which has been traced to a thorium content of about 0.02% on the basis of whole sand. It also contains about 0.4% of lithium and 0.3% of rubidium, which are distributed over both acid soluble and acid insoluble fractions. A proper mineralogical survey of the area at various depths including the shallower parts of the sea coupled with suitable methods of concentration, such as floatation and magnetic separation, could ultimately prove Clifton sand to be a valuable asset to the country. The technique of magnetic separation appears to be particularly attractive because a single pass through the separator

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has been found to double the concentraticns of iron, titanium, thorium, in the magnetic and of lithium in the non-magnetic fractions.

Chemical Analysis

Random samples of the sand drawn from the surface down to depths of about three ft. were analysed using both chemical and physical methods. In preliminary assays the percentage composition of the major constituents of the sand was found to be as noted in table I.

TABLE I.—COMPOSITION OF CLIFTON SAND

Moisture ..	1—2%
Material soluble in dilute HCl (10%)	24.80—26%
Fraction soluble in HCl under pressure includes that dissolved by cold dilute HCl (10%)	47—50%
Micaceous material obtained from $K_2S_2O_7$ fusion ..	43.8%—45%
Mica (by calculation) ..	10.1%—11%
Biotite and similar materials	45.5%—47%
Silica sand and dust ..	15%—16.17%
Calcareous material (calculated on the basis of loss in weight due to the evolution of carbon dioxide on addition of HCl)	20—22%

It will be seen that while the percentage of silica is remarkably low, that of the calcareous matter is exceptionally high. This feature of the sand and its general composition would seem to justify its descriptions as a mineral. Mica was identified under a polarizing microscope, while physico-chemical methods were used for identifying biotite and lepidolite. The calcareous material does not appear to originate from the weathering of limestone, which is abundant around the Karachi coast, but rather from the accumulation of the minute shells of dead sea-organisms as shown by microscopic examination (plate I).

The semi-quantitative estimation of mica was carried out by the following method. About one gram of the sand was fused with Na_2CO_3 and then extracted with HCl, the silica content being determined in the usual manner. The total quantity of silica so obtained is the sum of that obtained from mica, biotite, lepidolite, and silica present as such

Plate I.—Micro-photograph of non-magnetic fraction.

in the sand. Another sample of the sand (about one g.) was fused with potassium pyrosulphate and extracted with HCl ; the residue was then thoroughly washed with distilled water until free from chloride. The mica remains unattacked[3] and the residue obtained is a mixture of mica and silica (SiO_2 formed due to the decomposition of biotite and lepidolite, together with SiO_2 originally present). The difference between the two values gives the quantity of mica present in the original sand.

Qualitative analysis of the sand showed that it contains fair quantities of titanium, and lithium, in addition to iron, aluminium, calcium, magnesium, sodium, potassium, and silica and traces of thorium. These elements were estimated by the methods noted below :

1.	Iron	Volumetric	Dichromate.
2.	Titanium	Colourimetric	Pertitanic acid.
3.	Aluminium	Gravimetric	As oxide.
4.	Calcium	—do—	As carbonate.
5.	Magnesium	—do—	As pyrophosphate.
6.	Silica	—do—	Using hydrofluoric acid.
7.	Lithium	—do—	As sulphate.
8.	Thorium	(a) Geiger Counter. (b) X-ray fluorescence analysis. (c) Qualitatively as oxalate.	

A detailed account of the chemical constituents of the sand is given in tables (II to IV).

Spectroscopic & X-ray Analysis

The presence of lithium was confirmed by spectro-chemical analysis. The results of the chemical analysis were confirmed and supplemented (with special reference to thorium and titanium) by *fluorescent X-ray* analysis. (Plates II-A & B). The X-ray analysis also shows the presence of rubidium and strontium to the extent of 0.3% which could not, however, be detected chemically. Peaks corresponding to lithium, aluminium, and silicon are not observed in the X-ray spectrometer record, because these elements, being of low atomic weight, do not give characteristic X-radiation strong enough to be recorded with the usual apparatus. A rough estimate of the abundance of the elements was made from the peak heights. It is seen to be in substantial agreement with the chemically estimated values (table III).

Geiger Counter Analysis

Finally, the presence of the radioactive constituent was confirmed by means of Geiger counter measurements, and a quantitative

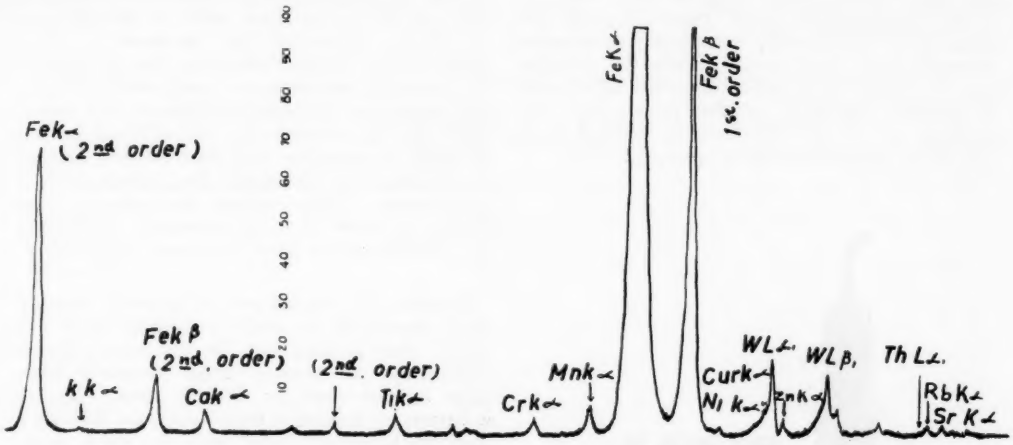

Plate II A.—X-Ray spectograph of the sand.

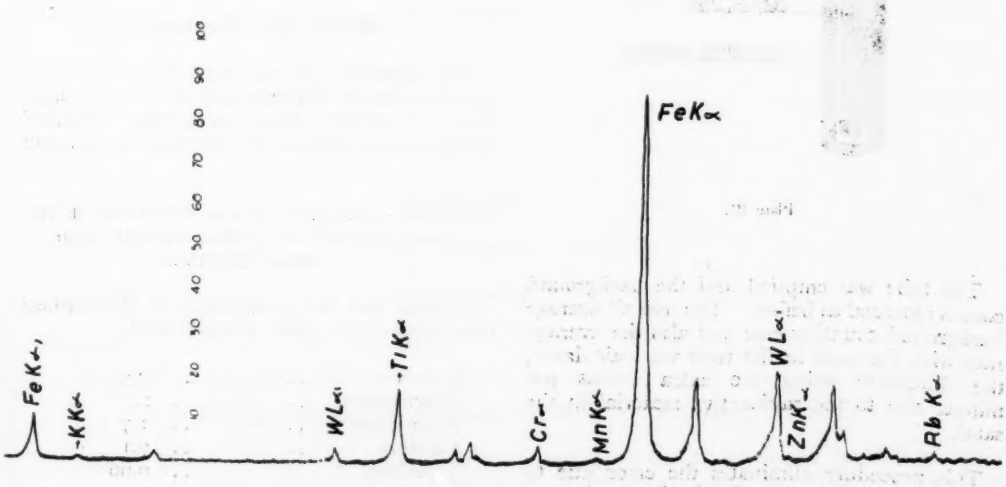

Plate II B.—X-Ray spectrograph of the sand.

estimate of thorium was made by comparing the radioactivity of the sand with standard radioactive samples. These standards were prepared as homogeneous mixtures of $CaCO_3$ with thorium nitrate and uranyl acetate by successive dilutions of thorium nitrate and uranyl acetate, respectively, with $CaCO_3$.

The method adopted for estimating the radiation given off by the sand was essentially to surround the counter tube by an annulus of the sand. Two tubes of transparent plastic with different diameters, closed at one and open at the other, were fitted into each other coaxially. The Geiger counter tube was inserted into the inner tube (plate III) and five readings of background counts of five minutes duration each were taken. Then the annular space between the plastic tubes was filled with a weighed quantity of the sand, and the number of counts obtained in several five-minute intervals was again recorded.

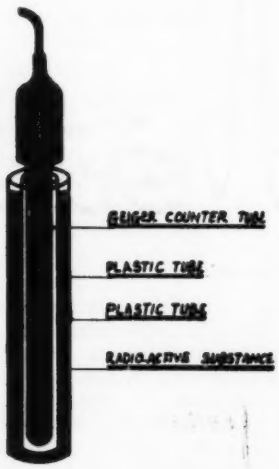

Plate III.

The tube was emptied and the background counts recorded as before. The overall average background counting rate and also the average rate with the sand in the tube was calculated, the difference being the extra counts per minute due to the radioactive material in the sand.

This procedure eliminates the error due to a possible variation in the background rate, extra counts (due to the sand) to be estimated to an accuracy of about 10% of the quantity measured. The counts for the standard materials were determined as in the case of sand. The weights of the various materials taken were nearly equal, varying from 70 to 75 grams. Since the standard contains a known quantity of thorium, the thorium content of the sand is readily estimated from the ratio of the counting rates.

Assuming that the radio-activity is distributed over a stretch of beach about 70 miles long, one furlong wide and about three and a half feet deep, it should contain approximately 30,000 tons of thorium, 800,000 tons of titanium and up to 50,000 tons each of lithium and rubidium. It is true that the sand is a low-grade source of these elements, but, in view of the growing importance of radioactive reserves and other rare elements in Pakistan, this source may not be insignificant. It will not be out of place to mention here that Atomic Energy Commission of America has announced a programme under which by-products containing as little as .05% uranium or thorium are considered as possible source materials.[4]

Further, the techniques of mineral dressing have developed to such an extent in recent times, that it may not be an impracticable proposition to recover these elements from poor sources such as Clifton sand. Out of a variety of available techniques, the following methods have been tried with this sand, particularly for the concentration of titanium, thorium and lithium.

Water Classification

The densities of the minerals of titanium and thorium are between four and five, whereas those of biotite, mica, calcareous material, lithium and rubidium ore are between 2.6 and

TABLE II.—ANALYSIS OF THE FRACTION OF THE SAND SOLUBLE IN HYDROCHLORIC ACID UNDER PRESSURE

(Values are the percentages of the cations calculated on the basis of whole sand)

Lithium	..	0.35
Magnesium	..	2.7
Aluminium	..	1.7
Calcium	..	7.1
Titanium	..	0.66
Iron	..	9.4
Thorium	..	Traces.

3.2. It was expected that with simple water classification, biotite, mica, lepidolite silica, and calcareous material would flow over, while thorium, and titanium minerals would sink to the bottom of the classifier, but the two fractions did not show any appreciable difference in their titanium and radioactive contents; the Geiger counter readings for both fractions were the same within the limits of experimental error.

TABLE III.—COMPARISON OE QUANTITATIVE ANALYSIS BY CHEMICAL MEANS AND A ROUGH QUANTITATIVE ESTIMATE FROM FLUORESCENT X-RAY ANALYSIS

(The values refer to the percentage of the elements present in the sand)

Element	Total sand		Micaceous material obtained after treatment of sand with HCl under pressure.	
	Chemical analysis	X-ray analysis	Chemical analysis	X-ray analysis
Lithium	0.35	——	——	——
Magnesium	2.8	——	0.31	——
Aluminium	5.1	——	7.1	——
Silicon	18.3	——	34.3	——
Calcium	7.3	5.0	0.24	——
Titanium	0.9	0.9	0.4	0.7
Chromium	not estimated	0.6	——	0.2
Manganese	not estimated	0.4	——	0.06
Iron	9.7	10.0	0.6	0.5
Nickel	——	0.2	——	——
Copper	——	0.06	——	——
Zinc	not estimated	0.04	——	0.05
Rubidium	not estimated	0.3	——	——
Strontium	not estimated	0.3	——	——
Thorium	Traces*	0.01	——	——

*Geiger counter measurements of table IV-√ 0.024% thorium.

Note : The low value for calcium as estimated from the X-ray record is probably due to calcium carbonate being in the form of granules, which are liable to loss during the preparation of the sample.

TABLE IV.—X-RAY COUNTS RECORDED WITH THE GEIGER COUNTER

	Back-ground	0.015% Uranyl acetate	0.1% Thorium nitrate	Clifton sand	Magnetic fraction	Non-magnetic fraction
Total counts per minute ..	6.0+0.5	27.7+1.1	23.3+1.1	16.0+0.8	19.3+0.8	13.4+.7
Counts after substraction of background ..	—	21.7+1.2	17.3+1.2	10.0+0.9	13.4+0.9	7.4+0.8
Equivalent radioactive content	— —	0.014% Uranium	0.42% Thorium	0.024% Thorium	0.033% Thorium	0.018% Thorium

Electromagnetic Separation

When the sand is passed through an electromagnetic classifier operating at a rather large flux density, the magnetic fraction is black in colour, and is found to contain silica, mica, lepidolite, and calcareous material.

The magnetic fraction gives considerable higher counting rate than the whole sand, about 70% of the original radioactivity being concentrated in this fraction, the rest being in the non-magnetic fraction. This result is rather surprising because monazite is not present in the sand, which is obvious from the X-ray spectrometer record, cerium being absent.

In the light of these observations it would appear that thorium in the magnetic fraction is present as intrusions[5] in the biotite, and the portion in the non-magnetic fraction is probably thorite resulting from the weathering and disintegration of biotite; it cannot be in the form of monazite or thorianite because in the X-ray analysis there is no indication of either cerium or uranium. The titanium appears only in the magnetic fraction (table V), so that its percentage in this fraction is about double that of in the whole sand. On the basis of these results it appears that titanium is either in the form of ilmenite or in combination with biotite.[6]

Further studies directed particularly towards the concentration of titanium, thorium, lithium and rubidium to economic limits, are in progress.

TABLE V.—CHEMICAL ANALYSIS OF MAGNETIC AND NON-MAGNETIC FRACTIONS OF THE SAND

Cations		Magnetic	Non-magnetic
Lithium	..	0.2%	.5%
Magnesium	..	5.4%	Traces.
Aluminium	..	6.6%	4.5%
Silicon	..	15.0%	17.5%
Calcium	..	0.40%	14.7%
Titanium	..	1.7%	Nil
Iron	..	17.2%	1.1%
Thorium	..	0.033%*	0.018%

*Estimated from Geiger counter measurements.

Acknowledgements

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References

1. Scotts Standard Methods of Chemical Analysis ; Text book of Quantitative Inorganic Analysis A.I. Vogal ; Text book of Quantitative Inorganic Analysis: Tred Well and Hall.
2. M. Mehmel., Chem. Erd., **11,** 307-32 (1937).
3. A. Wustfeld, Fortscher Gebiete Phosphatier, **3,** 137-41 (1950).
4. Clement J. Rodden, Arnal Chem. **21,** 327-35 (1949).
5. Giovanni Grocco. Rend Seminar. Facolta Sci. Univ. Cagliaria **20,** 298-32 (1950) ; Rend Coppens. Bull. Soc. franc. minerals **73,** 317-321 (1950).
6. S.R. Nockolds, Am. J. Sc., **145,** 401-20 (1947); R. Greenfell, Thomas, Thans, Proc. Roy. Soc. S. Australia, **48,** 258-68 (1924) ; F.F. Grout, Am. Mineral, **9,** 159-65 (1924).

STANDARDIZATION OF MYROBALAN EXTRACTS FOR THE MANUFACTURE OF FOUNTAIN PEN INKS

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THE indigenous manufacture of good-quality fountain pen inks is an important problem for the country, because approximately rupees five lakhs worth of these inks are presently being imported every year. A good ink should possess a number of properties such as good flow, a deep and fast colour, and freedom from corrosive action, sedimentation, and fungal growth. Of these, the last three conditions are critical and largely depend on the concentration and character of the organic acid used in the manufacture of the ink. This acid material is cheaply obtainable from the indigenous nut, *Myrobalan*, which is the name given to the unripe fruit or nuts of various species of the tree, *terminalia chebula*, of which the variety indigenous to Pakistan is known as "hurr". The nuts contain 30-40% tannin of the pyrogallol variety.

On hydrolysis of the aqueous extracts of these nuts, gallic acid solutions are obtained, which can be used in the preparation of inks of the ferrous-polyoxybenzene-complex type. For this, it is necessary to standardise these extracts in order to get a uniform, reproducible tinctogenic value of the ink.

The aqueous extracts of the nuts consist of mixtures of substances so numerous and chemically complex that, in our knowledge, there is no reference in the literature to practical methods for their separation or evaluation. The determination of tannin by the standard gelatin method does not afford a true criterion of the value of the product for ink making, and it was considered preferable to use the tinctogenic value itself for standardization.

As gallic acid is the main polyoxybenzene-compound in the myrobalan-tannins it was used for comparison as well as for fixing the optimum conditions under which the iron-complexes were formed.

Theoretically the formation of ferrous-gallic acid-complexes can depend on: (1) the molar ratio of ferrous salt to gallic acid ; (2) the pH of the solution ; (3) the nature of the buffer used ; (4) the time of formation; and (5) the temperature. It is also necessary to fix properly the conditions of the complex formation because the size of the particles in the colloidal solution of the blue iron complex should be within a definite range in order to get comparable tinctogenic values with photo-electric colorimetry. The necessary conditions for maximum sensitivity of photo-electric methods are the use of monochromatic light, the absence of large sized colloidal material in the solution examined, and an optimum thickness of the

absorption cell for maximum accuracy, the second of these conditions being amenable in the present case to only an approximate adjustment.

Ratio of the reactants: The colour developed from the equimolar mixture of ferrous-ammonium sulphate and gallic acid increases in intensity with further additions of the ferrous salt solution until a ratio of one part gallic acid to approximately eight parts of ferrous ammonium sulphate is obtained. A slight excess above this ratio does not appreciably vary the intensity of colour (*see* table IV). The spectral composition of colour is also not affected by small variations in the relative amounts of the reactants, though wide differences in the ratio do produce considerable alteration in the extinction coefficient, as will be seen from table I(a) and (b).

TABLE I(A).—EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS ACID COMPLEXES

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate in ml.	Extinction coefficient E × 100
1	0.5	4.0	13.0
2	1.0	8.0	28.0
3	1.5	12.0	54.0
4	2.0	16.0	76.0
5	2.5	20.0	98.0
6	3.0	24.0	111
7	3.5	28.0	118
8	4.0	32.0	122

TABLE I(B)

1	1.0	35.0	39.0
2	2.0	35.0	88.0
3	3.0	35.0	115
4	4.0	35.0	124

TABLE I(C).—EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES AT pH = 5.6

1	2.0	1.0	33.0
2	2.0	2.0	51.0
3	2.0	4.0	62.0
4	2.0	6.0	67.0
5	2.0	8.0	74.0
6	2.0	10.0	84.0
7	2.0	12.0	89.0
8	2.0	14.0	96.0
9	2.0	16.0	pptd.
10	2.0	18.0	pptd.

pH of the solution : Both the intensity and the composition of the colour are affcctcd by the pH of the medium (table II and V(a)-(*d*)), and the stability of the colloidal solution will also depend on this factor. It is therefore essential to fix the optimum pH to which the test solutions are buffered, within the acidic range in order to avoid oxidation of gallic acid.

Composition of the buffer : The requirements of a good buffer are a strong buffer-action and non-reactiveness towards the test substances. Both these conditions were best provided by the acetate buffer in the acidic range, while the boric acid-borax buffer of the same pH gave red instead of blue solutions, due to the well known formation of boron complexes with the hydroxylic compounds. (*see* table II(b)).

Size of the particles : A colloidal dispersion of the coloured precipitate changes the colour of the transmitted light and also reflects some of the light. In photo-electric colorimetry, the size of the particle therefore affects the estimation. With variations in the average size of the colloidal particles, there will be corresponding variations in the transmission of light. The size of the particles depends upon the concentration of the reactants, the method and order of mixing, and the time for which the solution is left standing. The preparation of the colloidal solution should be carried out in fair dilution because the sensitivity of the colorimeter rapidly decreases with the increase of extinction coefficient beyond about 0.5.

Time of standing of the colloidal solution : The colorimetric reading with a freshly prepared test sample goes on increasing with the time till a stage is reached where the extinction coefficient remains nearly stable for a long time (*see* table III). The readings have, therefore, been taken after the lapse of the time required for the attainment of the stability. This optimum time is influenced by pH of the medium, concentration of the reactants, and the temperature of the solutions.

Colloidal solutions tend to coagulate on standing, the size of the particles increasing due to the formation of agglomerates. The solutions should not, therefore, be left standing for unduly long periods before readings are taken.

Standardization—Method and Apparatus :

The "Series of Standards" method was considered to be of advantage, because it does not depend on the applicability of Beers' law. The maximum colouration developed with the known volume of the test substance is compared colorimetrically with a series of standards prepared with the same quantity of iron solution and increasing quantities of pure gallic acid solutions. The value of the unknown is measured against the standard to which it most nearly conforms and is estimated from that standard. When the volume and colour of the unknown sample and the standard are the same, the contents of the test substance in each will be identical, and its concentration in the sample is thus obtained without calculations.

A photoelectric colorimeter is used for observing the extinction coefficient of the various solutions. This apparatus is preferable to the visual method of observation with the Lovibond tintometer on account of its higher accuracy. Table I (c) shows how the extinction coefficient rises correspondingly with the concentration of the iron-complex-solution, while the visual tintometer gives no clear indication of the varying concentration of the iron-complex (Table II (c)). To obtain maximum sensitivity, a selected filter is placed in the path of the light before the photoelectric cell.

Experimental

Apparatus : The Gallenkamp photoelectric colorimeter was employed for determining the extinction coefficient of the solutions, while the Lovibond tintometer was used for the analysis of colour into its components.

Material : Pure gallic acid, acetic acid, sodium acetate, boric acid and borax, supplied by E. Merk, and ferrous ammonium sulphate of B.D.H. quality were used.

Ferrous ammonium-sulphate solution: Standard ferrous ammonium sulphate solution of M/40 strength was prepared by dissolving 1.7375 g. of the salt in distilled water and filling up to 250 ml. including 2.0 ml. of 10% hydrochloric acid to keep the solution free from turbidity.

Gallic acid solution : Gallic acid solution of M/40 strength was prepared by dissolving 1.1750 g. of gallic acid in distilled water and filling up to 250 ml. with distilled water. Three drops of toluene were added to keep it free from moulds.

Acetic acid — Sodium acetate buffer :

(*a*) *Acetic acid solution* of molar strength was prepared by volumetric standardization method.

(*b*) Molar sodium acetate solution was prepared by dissolving 136.0 g. of the salt (with 3 moles of water of crystal ization) in distilled water and making up to one litre.

Boric acid — Borax buffer :

(*a*) 12.404 g. of boric acid plus 2.925 g. sodium chloride was dissolved and made up to one litre with distilled water.

(*b*) 19.108 g. of borax was also dissolved in distilled water and made up to one litre.

Buffers of various pH values were made from these solutions in accordance with "International Critical Tables" Vol. 1, pp. 81-84.

Preparation of the Extract

The nuts, obtained from the local market, were ground and sifted through a 10-mesh sieve.

One hundred grammes of the sifted powder was packed in a large separating funnel having a cotton plug at the bottom and hot water was allowed to percolate slowly through it. The end of the extraction was determined by the formation of only a negligible blue colour on adding an excess of ferrous ammonium sulphate solution to a few ml. of the extract. Three liters of hot water (at 70°-80°C.) were necessary for the complete extraction of tannin.

Hydrolysis of the extract : Five hundred ml. of the extract was refluxed with 25.0 ml. of 10% hydrochloric acid for eight hours to hydrolyze the gallotannin, cf. the method recommended by G. Martin and E.I. Cooke (Industrial Chemistry : Organic, seventh edn., p. 490, 1952, The Technical Press Limited, London).

Selection of the filter : The test solution was taken in an observation tube and colorimetric readings with different filters placed in the path of the light were recorded, the maximum reading being observed when filter "608" was used. Filter "608" was therefore employed during all the observations for the colorimetric readings.

TABLE II (A).—pH VALUES OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES WITH DIFFERENT BUFFER SOLUTIONS

Cylinder No.	pH of the buffer solution (10.0 ml.)	M/40 gallic acid soln in ml.	Iron solution (M/40) in ml.	pH of the colloidal solution
1	3.6	2.0	2.0	3.6
2	3.8	,,	,,	3.8
3	4.0	,,	,,	4.0
4	4.2	,,	,,	4.2
5	4.4	,,	,,	4.4
6	4.6	,,	,,	4.6
7	4.8	,,	,,	4.8
8	5.0	,,	,,	5.0
9	5.2	,,	,,	5.2
10	5.4	,,	,,	5.4
11	5.6	,,	,,	5.6
12	6.77	,,	,,	6.77
13	7.60	,,	,,	7.60
14	8.08	,,	,,	8.08
15	8.69	,,	,,	8.69

(*i*) *Determination of the optimum pH :* A series of fifteen 100 ml. cylinders were arranged and 10.0 ml. of different buffer solutions of pH values varying from 3.6 to 8.69 were taken. For the pH values from 3.6 to 5.6, acetic acid-sodium acetate buffers, and from 6.7 to 8.69 boric acid-borax buffers were used. Two ml. of M/40 gallic acid solution was added to every cylinder and the volume made upto 60 ml. by adding distilled water. Two ml. of M/40 ferrous ammonium sulphate solution was added to each and the final volume was adjusted to 100 ml. The pH of the solutions was not affected, and still corresponded to the values of the buffers taken in each case (table II(a)).

Tintometer measurements on the fifteen samples showed that the composition and intensity of colour remained practically constant when the pH of the medium was 5.2-5.6. (Table II(b)). In this range of pH values, the blue component increased very slightly while the yellow component remained constant. There was no regularity in the composition and intensity of colour in the pH range 6.70-8.69. The colour of the solutions in this pH range was predominantly red instead of blue, due to the formation of the already mentioned boron complexes.

TABLE II (B).—LOVIBOND VALUES OF THE COLLOIDAL SOLUTIONS OF FERROUS-GALLIC ACID COMPLEXES

Cylinder No. cf table II(a)	pH of the colloidal solution	Red	Yellow	Blue
8	5.0	(7.0 (6.8	(8.0 (8.0	(11.6 (11.0
9	5.2	(7.1 (7.1	(8.0 (8.0	(9.2 (9.4
10	5.4	(7.2 (7.1	(8.0 (8.0	(8.6 (8.8
11	5.6	(7.2 (7.3	(8.0 (8.0	(8.3 (8.3
12	6.77	(4.1 (4.0	(3.0 (3.0	(4.8 (4.8
13	7.60	(12.4 (12.4	(6.0 (6.0	(9.6 (9.4
14	8.08	(11.2 (11.3	(7.0 (7.0	(9.0 (9.0
15	8.69	(9.9 (10.1	(7.0 (9.0	(7.3 (7.3

TABLE II (c).—LOVIBOND VALUES OF THE COLLOIDAL SOLUTIONS OF FERROUS-GALLIC ACID COMPLEXES CONTAINING 2 ML. OF M/40 GALLIC ACID SOLUTION

Cylinder No. cf. table I(c)	M/40 ferrous ammonium sulphate solution in ml.	Red	Yellow	Blue
1	1.0	4.4	1.4	5.3
2	2.0	6.5	1.6	6.9
3	4.0	8.0	3.9	10.8
4	6.0	9.2	3.9	11.2
5	8.0	7.1	3.1	9.5
6	10.0	7.0	5.7	11.1
7	12.0	8.0	7.1	12.2
8	14.0	7.5	7.6	11.8
9	16.0	7.0	6.3	10.7
10	18.0	7.0	6.9	10.5

The time required for the full development of colour was longer with solutions at lower pH values. It was visually observed that solutions buffered at pH 5.2 to 5.6 developed strong colour within a minute while solutions at pH values below 4.4 required more than five minutes to develop a colour of similar strength. It was also observed that tendency towards coagulation of the colloidal solutions increased with decreasing pH of the solutions. Colloidal solutions buffered at pH 5.6 were clear even after standing for five days, while solutions at lower pH values had coagulated.

Due to the above considerations, pH 5.6 was considered to be the optimum pH to which all of the test solutions were buffered.

(ii) Determination of the time of standing : Colloidal solutions of two strengths buffered at pH 5.6 were prepared : (A) 0.25 ml. of the gallic acid solution mixed with 8.0 ml. of the ferrous ammonium sulphate solution and diluted to 100 ml. ; and (B) 0.5 ml. of the gallic acid solution mixed with 16.0 ml. of the ferrous ammonium sulphate solution, and diluted to 100 ml. The colorimetric readings were recorded every five minutes until relatively stable values were obtained, after a lapse of about 50 minutes (figure 1) ; the readings increased monotonously in both cases (table III and curves of figure 1).

TABLE III—TIME FOR THE CONSTANT VALUES OF THE EXTINCTION COEFFICIENT OF TWO COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES OF DIFFERENT STRENGTHS

Time interval in minutes	Extinction coefficient E × 100	
	Solution A	Solution B
10	45.0	72.0
15	49.5	75.0
20	53.5	76.0
25	55.5	76.5
30	58.0	80.0
35	59.0	81.0
40	60.0	82.0
50	61.5	84.0
60	62.5	85.0
70	63.5	85.5
80	64.5	—

Solution A:—0.25 ml. M/40 gallic acid and 8.0 ml M/40 ferrous ammonium sulphate.
Solution B:—0.5 ml. M/40 gallic acid and 16.0 ml M/40 ferrous ammonium sulphate.

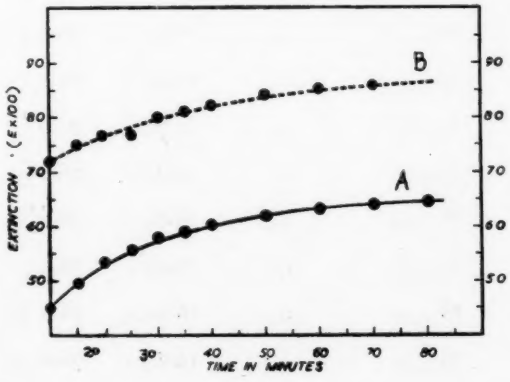

Fig. 1.

(iii) Ratio of the reactants : 10.0 ml. of the buffer of pH 5.6 were taken in each of the 19 cylinders of the series. Two ml. of M/40 gallic acid solution was added to each and the volume made upto 60 ml. M/40 ferrous ammonium sulphate solution was added in increasing steps of 1.0 ml. to every cylinder of the series, the volume being then made upto 100 ml.

TABLE IV

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	2.0	1.0	10.5
2	,,	2.0	25.0
3	,,	3.0	34.0
4	,,	4.0	45.0
5	,,	5.0	55.0
6	,,	6.0	57.0
7	,,	7.0	60.0
8	,,	8.0	69.0
9	,,	9.0	61.0
10	,,	10.0	65.0
11	,,	11.0	58.0
12	,,	12.0	68.0
13	,,	13.0	64.0
14	,,	14.0	71.0
15	,,	15.0	76.0
16	,,	16.0	76.0
17	,,	17.0	76.0
18	,,	18.0	76.0
19	,,	19.0	76.0

The time required for the attainment of the relatively stable colour determined experimentally with the first and the last samples of the series was found to be about 40 minutes. Readings were therefore taken after 50 minutes. The extinction values increased with the increase in the quantity of ferrous ammonium sulphate solution. Samples with more than 15 ml. of the ferrous solution gave nearly constant values. It was found that 1.0 ml. of M/40 gallic acid solution needed at least 7.5-8.0 ml. of M/40 ferrous ammonium sulphate solution to give the maximum colouration at pH 5.6 and temp. = 30°C. (table IV).

Similar experiments were carried out at different pH values, and it was observed that although the maximum readings obtained were influenced by the pH of the solution (lower extinction coefficients in the case of lower pH values), the optimum ratio of the reactants was approximately the same (table V).

TABLE V(A).—at pH=4.4

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	0.5	1.0	19.0
2	,,	2.0	25.0
3	,,	3.0	30.5
4	,,	4.0	33.5
5	,,	5.0	36.5
6	,,	6.0	36.5

TABLE V (B).—at pH=4.8

1	0.5	1.0	30.0
2	,,	2.0	37.0
3	,,	3.0	40.0
4	,,	4.0	41.0
5	,,	5.0	41.0
6	,,	6.0	41.0

TABLE V (C).—at pH=5.2

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	0.5	1.0	40.0
2	,,	2.0	42.0
3	,,	3.0	43.0
4	,,	4.0	44.0
5	,,	5.0	45.0
6	,,	6.0	46.0

TABLE V (D).—at pH=5.6

1	0.5	1.0	42.0
2	,,	2.0	42.0
3	,,	3.0	46.0
4	,,	4.0	46.0
5	,,	5.0	46.0
6	,,	6.0	49.0

(iv) Standardization of the hydrolyzed myrobalan extract : Ten ml. of the buffer of pH 5.6 was taken in every cylinder of the series, 0.5 ml. of the extract was added to each, and the volume was made upto 60 ml. M/40 ferrous ammonium sulphate solution was added to each in increasing steps of 2.0 ml. The solutions were mixed slowly with constant stirring.

The first and the last samples of the series were observed colorimetrically at intervals of five minutes. The time required for the full development of colour was nearly 30 minutes. The final readings of the whole series were therefore taken after 40 minutes. The readings were constant at 83.0 with the solutions having 10.0-16.0 ml. of iron solution (table VI (a)).

In another series of eight cylinders 10.0 ml. of the same buffer (pH 5.6) were taken and M/40 gallic acid solution was added in increasing steps of 0.05 ml. The readings were recorded as in the last experiment. The extinction value of the series which corresponded to the extinction value of the extract was noted against the standard with 1.70 ml. of the gallic acid solution (*see* table VI b). It

TABLE VI (A)

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES OBTAINED WITH HYDROLYZED TANNIN EXTRACT

Cylinder No.	Hydrolyzed tannin extract in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	0.5	2.0	74.5
2	,,	4.0	78.5
3	,,	6.0	80.0
4	,,	8.0	83.5
5	,,	10.0	84.0
6	,,	12.0	83.0
7	,,	14.0	85.0
8	,,	16.0	84.5

TABLE VI (B)

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES

Cylinder No.	M/40 gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	1.50	10.0	74.0
2	1.55	,,	77.0
3	1.60	,,	79.0
4	1.65	,,	80.0
5	1.70	,,	83.0
6	1.75	,,	86.5
7	1.80	,,	85.5
8	1.85	,,	92.5
9	1.90	,,	94.0

follows from this that 0.5 ml. of the hydrolyzed extract is equivalent in its colour value to 1.70 ml. of M/40 gallic acid solution. The strength of the extract in terms of the gallic acid equivalent was thus found to be 16 g./litre, *i.e.*, M/12 approximately.

The accuracy of this method was estimated at 0.05 ml. in 1.70 ml., which means approximately 3% by volume, so that a difference of 0.04 grammes of gallic acid can be detected. Table VI (b) shows that the accuracy can be improved by interpolation between standards, because an alteration of 0.05 ml. in the volume of gallic acid solution produced 2.5 units difference in the extinction coefficient. On the other hand, there is a drawback in the method, in so far as the size of the particles as well as the stability of the complexes varies uncontrollably over a small range, affecting the accuracy adversely to the extent of about 2%, so that nothing could be gained by improving the accuracy of the measurements beyond that limit.

STUDIES ON SHARK LIVER OIL

Part 1—Physico-chemical Constants and Vitamin 'A' Content of Liver Oil from Sharks of the Karachi Coast

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FISH liver oils have attained great commercial importance on account of being rich sources of vitamins A and D. In many countries of Europe and America large industries developed and exploited different fishes like cod, halibut, sword-fish etc., for this purpose. During the past few years Pakistan has imported on an average 200,000 pounds a year of low potency fish liver oils at a cost of approximately Rs. 400,000. To this must be added the imports of vitamin concentrates at a still higher cost in foreign exchange. Unfortunately no such industry exists in Pakistan although marine fishes abound along the Karachi and Makran coasts. According to the statistics collected by the Central Fisheries Department, the present landing of sharks has been continuous over a period of years and stands around 10,000 tons per annum. Considerable amount of shark meat is dried, cured and exported from this country, but the liver oil is extracted in a very crude manner, resulting in a dark coloured obnoxious smelling product which is mainly used for smearing fishing boats.

In view of the facts stated above systematic investigations on the problem have been taken up. The present paper deals with the yields and the physico-chemical characteristics of the oils from different species of sharks, and their vitamin A content in relation to age, size and sex of the fish. It may be stated in this connection that the liver oil of sharks found in Indian waters has been studied by Chakarwarty, Sarangdhar, Kini, Setna, Das and others [1-6] but sharks of the Karachi coastal waters have not been paid much attention, and there are only a few isolated references on the yields of their liver oil and its vitamin A content.

In the course of the present studies the following conclusions have been arrived at :—

(1) The oil extracted from various species of sharks contains from 2000 to 72,000 U.S.P. units of vitamin A per gram with an average of 15,000 U.S.P. units per gram, which is a much higher average than is noted for the liver oil of sharks from any other coastal area of the sub-continent. According to Setna[4] this is perhaps due to the super-abundance of prawns and shrimps on the Karachi coast and the comparative

PHYSICO-CHEMICAL CONSTANTS AND VITAMIN 'A' CONTENT OF LIVER OIL FROM SHARKS OF THE KARACHI COAST

Date of collection	Name of Fish	Sex	Approx. body weight lbs.	Length Ft.	Weight of Liver lbs.	Liver oil %	Vitamin 'A' U.S.P. units per gram.	Free fatty acids as oleic %	Unsaponifiable matter %	Saponification value	Iodine value	Refractive index at 40°C.	Specific gravity at 30°C.
	Hammerhead Sharks												
15- 2-56	Hammerhead shark (unidentified sp.)	Male	—	—	—	36.5	54,000	0.4	4.7	177.0	150.6	—	—
5- 5-56	Sphyrna malleus. 'Bodher-buther'	—	—	3	3.5	21.3	53,300	0.7	—	—	—	—	—
19- 9-56	—do—	Female	160	10	16	40.2	11,618	0.1	3.8	175.0	124.0	1.4662	0.9183
23-10-56	—do—	Female	15	4	0.7	6.0	18,000	0.2	—	184.0	—	—	0.9173
10- 1-57	—do—	Male	160	5.5	6	38.5	72,359	0.13	6.1	183.1	131.2	1.4670	0.9151
13- 2-57	—do—	Male	200	12	30	46.0	40,222	0.4	5.7	183.1	—	1.4671	0.9121
5- 6-56	Sphyrna blochii 'Julia mangar, Doka'	Male	15	2	0.7	10.0	51,000	0.7	—	—	—	—	—
14-11-56	—do—	Female	280	6.5	20	20.6	71,500	1.4	7.7	177.2	129.3	1.4685	0.9165
10- 1-57	—do—	Male	14	4	1.2	15.6	18,198	0.13	3.7	184.9	113.0	1.4670	0.9161
	Saw Fishes												
1- 2-56	Pristis cuspidatus .. .. 'Khanda mangar, Liaro'	—	—	—	—	10.6	8,800	0.4	2.7	182.2	151.1	1.4660	0.9191
25- 9-56	—do—	Female	120	6	8	33.1	5,640	0.29	3.9	184.0	133.0	1.4662	0.9196
3-11-56	—do—	Female	100	7	4.5	24.8	9,227	0.13	2.8	193.1	146.2	1.4660	0.9188
27- 8-56	Pristis zysron 'Kharra mangar'	Female	50	5	2	9.5	2,708	0.17	2.5	183.9	—	1.4665	0.9170
4- 9-56	—do—	Male	1600	20	160	59.1	8,200	0.1	3.6	185.6	105.0	1.4613	0.9143
25- 9-56	—do—	Female	160	9	13	34.8	1,829	0.39	3.7	186.0	142.9	1.4648	0.9176
	Skates												
25- 2-56	Rhinobatus granulatus 'Kair, Seroe'	Female	—	—	—	36.3	14,000	0.15	2.2	181.0	145.1	1.4664	0.9182
2- 1-57	—do—	Female	30	4	1	8.1	7,876	0.09	3.4	172.2	152.0	1.4650	0.9195
1-11-56	Rhynchobatus djeddensis ..	Female	80	5	2	21.3	3,274	0.1	4.7	180.1	131.1	1.4685	0.9220
3-11-56	—do—	Female	50	5	1.6	30.0	3,927	0.07	6.0	187.1	113.5	1.4682	0.9212
27- 8-56	Unidentified sp.	Female	30	4	2.5	20.2	2,369	0.16	2.1	185.0	—	1.4660	0.9200
	Miscellaneous Sharks												
5- 6-56	Carcharias limbatus .. .. Small black tipped grey shark. 'Muyyach'	Female	80	5	7	38.5	4,100	0.10	1.9	172.0	141.1	1.4640	0.9171
17- 7-56	—do—	Male	100	6	10	30.0	19,000	0.13	—	183.0	—	1.4654	0.9188
3-11-56	—do—	Female	80	6	4.2	12.9	6,693	0.49	4.17	189.9	121.3	1.4668	0.9193
25- 6-56	Carcharias melanopterus .. Large black tipped grey shark. 'Kanatyan ; 'hangar'	Male	20	2.5	—	23.0	21,300	0.39	4.3	177.0	100.2	1.4668	—
17- 7-56	Rhineodon typicus Whale shark, 'Mohr mangra' ..	Female	30	3.5	2	36.0	2,050	0.16	1.3	185.0	—	1.4593	0.9170
15-10-56	—do—	Female	8	3	0.5	10	750	0.19	—	177.1	123.0	1.4635	0.9175
24- 7-56	Galeocerdo arcticus Tiger shark, 'Kari'	Male	4	2	35gm.	39.9	7,140	2.4	6.3	180.0	147.0	—	Oil was
24- 7-56	—do—	Female	4	2	30gm.	41.0	2,300	2.5	10.9	187.1	135.2	—	extracted
15- 2-57	—do—	Male	200	10	50	65.5	21,682	0.27	—	192.0	122.0	1.4630	by means of ether

dearth of this important fish food near Bombay.

(2) Hammerhead shark (*S. malleus*) is the richest source of vitamin A. Its liver oil contains up to 72,000 U.S.P. units of vitamin A per gram. The yield of oil from adult sharks ranges from 21-46% of the weight of fresh liver. Liver of males have a higher vitamin content than those of females.

(3) Maturity of the fish and size of the liver have an important bearing on the yield of oil. Large livers weighing 6 lbs. or more yield 30-65% and small livers only 8 to 25% of oil.

(4) The chemical constants of the oil such as iodine value, saponification value and the percentage of unsaponifiable matter significantly vary with the different species of sharks, whereas physical constants *i.e.*, specific gravity and refractive index show only slight differences. No correlation was found between any of the physico-chemical constants and vitamin A potency. The unsaponifiable matter of the oil has a much lower percentage (1.3 to 10.9%), compared to liver oils of sharks of the Atlantic and Pacific coasts for which it has been recorded upto 90%.

The shark was identified and the necessary data regarding the sex, approximate body weight, the weight of the liver and length of the fish were noted. The liver was brought to the laboratory and after removing blood, gall bladder etc. was minced in a mincing machine. Weighed quantity of liver was mixed with twice its weight of hot water and digested for about 45 minutes at 80-85 °C. The mixture was allowed to stand for some time in a separating funnel. The lower layer of water was removed and the oil along with the liver tissue was centrifuged. The oil thus separated was finally dried over anhydrous sodium sulphate and filtered hot into a tared flask. Vitamin A was determined spectrophotometrically[7] and physico-chemical characteristics of the oil were determined by standard methods and are recorded in the attached table.

References

1. Chakarwarty et al., J. Ind. Chem. Soc., **10,** 361 (1933).

2. Sarangdhar, Ind. J. Med. Res., **30,** 553-60 (1942).

3. Kini, J. Indian Chem. Soc., Ind. Edn, **7,** 32 (1945).

4. Setna, J. Sci. and Ind. Res. (India), **3,** 303, (1945).

5. Sarangdhar, J. Sci. Ind. Res. (India), **6B,** 180-5 (1947).

6. Das et al., Proc. Indian Acad Sci., **29B,** 13-22 (1949).

7. *Methods of Vitamin Assay*, ed. by Association of Vitamin Chemists, Inc., Interscience Publishers, Inc., New York, N. Y., 1951, pp. 36-39.

INSULIN CONTENT OF PANCREAS FROM LAHORE SLAUGHTER HOUSES

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THE insulin content of pancreas of animals slaughtered in local slaughter houses has been studied with a view to examine the possibility of producing insulin locally—because of the difficulty in the availability of this essential product. It is well known that a number of factors such as the species of the animal, health, age, climate and season, affect the insulin content of the pancreas. No studies of the insulin content of locally available pancreas have, hitherto, been made in this country. These are of interest, even if the industrial production of insulin may not be economically feasible, for conditions of scarcity of this drug continue to occur periodically.

In Lahore there are two slaughter houses, one for beef and the other for mutton. In the beef slaughter house 80 to 100 animals are slaughtered five times a week, while in the mutton slaughter house 800 to 1200 animals are slaughtered in the same period. Cows, oxen, bulls and buffaloes are slaughtered in the beef slaughter house, while different species of goats and sheep are slaughtered in the mutton slaughter house.

The animals slaughtered in the beef slaughter house are such as have become otherwise uneconomical to maintain and are often old and in a poor state of nutrition. These are required by law to be over ten years of age or otherwise declared unfit for any other purpose. The animals slaughtered in the mutton slaughter house are generally young but often quite lean since they are driven from long distances to the city for slaughter. This long walk of a week or ten days with scarcity of food on the way make them physically frail at the time of slaughtering.

Pancreas of animals were collected under suitable conditions immediately after slaughtering and examined for insulin content. A number of relatively pure preparations of insulin were made from the extracts of the pancreas during the course of the work, but these were found to lose some of the insulin activity during the process. It was, therefore, found more convenient to assay suitable extracts directly without any elaborate treatment for purification. These were assayed using rabbits as experimental animals. The yield of insulin has been expressed in units per kilogram of pancreatic tissue.

Extract Preparation

Insulin extracts were prepared by the method of Hinkel and Maxwell.[1] The processing was done within an hour of the slaughter of the animals as otherwise the yield of insulin was found to be lowered even when the pancreas were rapidly chilled. This is in conformity with the earlier work.[2,3]

Five hundred grams of the defatted, minced pancreas were added to 1,500 ml. of 85% alcohol containing 25 ml. of phosphoric acid to give a pH 3.0. This was vigorously shaken mechanically for three hours, centrifuged and re-extracted under similar conditions. The combined extracts were made alkaline to pH 8.2 with NH_4OH, filtered and reacidified to pH 3.5 with H_2SO_4. After concentration in vacuo at 20°C., to a volume of 500-600 ml. the residue was filtered off and the clear solution used for assay of insulin.

Methods for the standardization of the insulin extracts generally make use of mice or rabbits as experimental animals.[4] The mouse is easier to handle and has, therefore, replaced the rabbit in most laboratories but due to the non-availability of a suitable strain of white mice we used rabbits in this study. The method we followed is described by Marks.[5] For each test, eight rabbits were used. These were maintained on a diet of chick pea, green vegetables, and grass. Before the actual tests, the animals were made to fast for 20-24 hours. After each test they were given a rest of three to six days before the cross-over test. Blood was collected from the ear veins in oxalated capsules.

Reference Standard

Unfortunately at the time of these experiments we did not have a standard insulin preparation. We used for comparison a preparation of insulin manufactured by Eli Lilly and Co, Indianapolis, marked as containing 40 units per ml. We hoped to standardise this preparation against a proper standard at a later stage. This solution was diluted with

distilled water containing 0.3% cresol and 0.85% NaCl and pH adjusted to 2.5 so that the diluted solution contained one unit of insulin per ml. This was used as a standard for comparison.

The method of Hagedorn-Jensen[6] as adopted by Marks[4] was used for the estimation of blood sugar. Marks[4] had used 0.005 N sodium thiosulphate solution for titration, but we found it more convenient to use a solution of 0.001 N strength, which resulted in the greater accuracy of results in our hands. The method was standardised using a glucose solution of known strength.

Conclusions

A number of extracts were prepared in the manner described above both from beef and mutton pancreas and assayed. The results of ten representative samples are shown in the table I.

The results summarised in the above table show that insu'in content of beef pancreas examined, range from 892-1002 units per kg. and that of mutton pancreas from 585-695 units per kg. These yields are much lower than t hose reported in the literature for the pancreas of normal animals of these species.

TABLE I

INSULIN CONTENT OF BEEF PANCREAS

No.	Weight of minced pancreas (g.)	Vol. of the final extract (ml.)	Pancreas extract: Dose per animal (ml.)	Pancreas extract: Total reduction in blood sugar (%)	Standard preparation: Dose per animal (units)	Standard preparation: Total reduction in blood sugar (%)	Response ratio	Potency of the sample with respect to standard (%)	Calculated potency of the extract (units/ml.)	Insulin content of the pancreas (units/kg.)
1.	500	535	1.0	66.90	0.5	246.10	27.2	33.07	0.1654	179
2.	500	630	1.0	297.71	0.5	242.26	122.88	141.58	0.7079	892
3.	500	675	0.5	202.08	0.5	261.05	77.4	70.9756	0.710	959
4.	500	480	0.5	256.12	0.5	248.98	102.86	104.4415	1.044	1002
5.	500	500	0.5	230.06	0.5	248.45	92.598	89.362	0.8936	894

INSULIN CONTENT OF MUTTON PANCREAS

1.	500	800	1.0	212.37	0.5	234.06	90.73	86.86	0.4343	695
2.	337	500	1.0	111.82	0.5	233.01	47.989	45.366	0.2268	337
3.	500	300	0.5	250.27	0.5	254.02	98.87	98.2965	0.983	590
4.	500	580	1.0	248.39	0.5	240.33	103.35	105.22	0.5261	610
5.	500	600	1.0	252.88	0.5	257.30	97.42	97.42	0.4871	585

Inspite of our best efforts it was not possible for us to process the pancreas in less than one hour after the slaughter. It is possible that some loss of insulin occurred during this time on account of enzyme action. The insulin content of mutton pancreas is found to be much lower as compared with that of beef pancreas. Even the values of beef pancreas are low as compared to data reported by Fischer and Scott,[7] given below in table II.

TABLE II

Animal	Age	Units of insulin per kg. of pancreas
Foetal calves ..	5 months	29,000—38,800
Foetal calves ..	5-7 months	21,100—24,900
Calves ..	6-8 weeks	10,400—12,800
Cattle ..	2 years	3,900— 6,100
Cows ..	9 years	1,700— 2,000

It has been estimated that the slaughter houses of Lahore which provide about 30-40 kg. weight of the pancreas per day can yield about 30,000 units of insulin per day. This figure is too low to justify the production of insulin on a commercial basis. However, since the total number of animals slaughtered in the country in different slaughter houses is very large, there still remains the possibility that if the slaughter houses are scientifically organised, and freezing facilities provided, the production of insulin and even of other glandular products may come within the range of feasibility.

References

1. L.C. Maxwell and W.P. Hinkel, Chem. Abstracts, **46,** 7293 b (1952).
2. J.J.R. Macleod, J. Metabolic Research, **2,** 149 (1922).
3. F.G. Banting and C.H. Best, J. Lab. Clin. Med., **7,** 464 (1921-22).
4. J.H. Burn and others, *Biological Standardization,* Oxford Medical Publications, London, 1950.
5. H.P. Marks, *League of Nations Report of Insulin Standardization,* C.H. 398, 1926.
6. Hagedorn and Jensen, Biochem. Zeit., **135,** 46 ; ibid., **137,** 92, (1923).
7. A.M. Fisher and D.A. Scott, J. Biol. Chem., **106,** 305 (1934).

GLUTAMIC ACID

Possibilities of its Production in Pakistan and its Uses

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GLUTAMIC acid is one of the essential amino acids. It plays a central role in the intermediary metabolism. It is used in limited quantities as a drug in the treatment of mental deficiencies and for other medicinal purposes. Apart from its use as a constituent of food, it has recently been employed in depilatories[2] and hair-wave lotions to protect hair from damage. Glutamic acid hydrochloride is used to aid the production of a non-corrosive solder flux. Sodium salt of glutamic acid has been extensively employed in Japan and China for use as a food condiment. The condiments variously known as "Aji-no moto", "Ve-tsin" etc. are principally monosodium glutamate mixed with about 10-20% sodium chloride.

Glutamic acid was first isolated from proteins in 1866 by the German chemist Ritthausen,[3] and synthesized by Wulff,[4] in 1890. Compared to its production from proteins, the presently known synthetic methods are much more costly, intermediate yields are lower and the product obtained is usually the racemic inactive form which is difficult to convert into the active or dextro configuration.

In 1912, Ikeda[5] hydrolyzed a seaweed (*Laminaria japonica*) and separated glutamic acid from other amino acids. On neutralization with soda, the sodium glutamate was found to possess a desirable meat-like taste. Since then, it found its way into the culinary formulae of Japan and China. It was patronized by the public to such an extent that in 1930 its production in China rose to 350,000 pounds. A few years later, the Chinese material was beginning to compete with the Japanese product in Singapore, Malaya and the Philippines. The interest in the material rose in the United States during and since World War II from when it became available in abundance. It is mainly used by the food canning and dehydration industries.

Almost all proteinous materials contain variable quantities of glutamic acid. But wheat gluten, corn gluten, extracted soyabean flour, casein, peanut flour, yeast, dried distiller's solubles, extracted cottonseed meal and fish waste are a rich source of the acid. Other proteins such as egg albumen can also be used for making glutamic acid. The gluten proteins, however, are unique in the sense that they contain a very high percentage of glutamic acid as is clear from table I.[6]

TABLE I

Amino Acids	*Percentage*
Alanine	9.8
Arginine	1.5
Aspartic acid	1.7
Cystein	1.2
Glutamic acid	20.1-24.0
Glycine	0.4
Histidine	0.8
Isoleucine	3.7
Lysine	6.1
Methionine	2.0
Phenylalanine	6.6
Threonine	3.0
Tryptophane	Trace
Tyrosine	2.6
Valine	1.9

Use as Food Flavour

Pure monosodium glutamate possesses a meat-like taste, but essentially no odour. It is used in the preparation of certain soups and gravy flavourings. It can be used in water as a substitute for beef tea. It cannot, however, supplant meat. Monosodium glutamate suppresses undesirable sharpness in onion flavour, rawness in many vegetables and some meats, flavour of peel and earthiness in vegetables, particularly in potatoes, a volatile

characteristic note in boiled rice, bitter tastes in freshly opened canned vegetables, a fishy odour sometimes present in lima beans and bitterness in saccharine solutions are also dulled by the use of monosodium glutamate. A mixture containing sodium glutamate 1.787 g., NaCl 550 g. protein hydrolysate 257 g., and glutamic acid 137 g., in a wafer or chewing gum[7] taken 15 to 30 minutes before meal time suppresses the appetite. The flavour in the mouth is responsible for the feeling of fullness.

Production

For the production of glutamic acid on an industrial scale, gluten—a by-product of starch industry—is used for it is a cheap proteinous material. Wheat gluten which contains from 80 to 90 per cent protein, is a good source on account of its high glutamic acid content. Hydrochloric acid is generally the hydrolyzing agent for food hydrolysates. Gluten and hydrochloric acid are usually heated in the presence of a small quantity of finely granulated tin. The tin[8] accelerates the hydrolysis and removes any arsenic present. The solution is filtered, concentrated under reduced pressure, and the glutamic acid hydrochloride allowed to crystallize. The crude crystals are dissolved in water and neutralized with sodium hydroxide to pH 3.2 [9] to get glutamic acid. The glutamic acid slowly crystallizes out over a period of several days. It can be converted to monosodium glutamate by dissolving it in water and by neutralizing with sodium hydroxide to pH 5.4-6.2.

The glutamic acid and its sodium salt were prepared by hydrolyzing wheat gluten, maize and casein with hydrochloric acid. The yields under different conditions of time and acid concentration have been summarized in table II. It is clear that with wheat gluten, hydrochloric acid of specific gravity 1.18 gives the best yields when the hydrolysis is conducted for six hours. With maize gluten, the most favourable conditions are :—specific gravity of HCl 1.14, and duration of hydrolysis 12 hours.

Manufacture in Pakistan

The most important pre-requisites for the commercial production of glutamic acid in Pakistan are :—

(*a*) abundant supply of proteinous materials rich in glutamic acid ;
(*b*) cheap supply of hydrochloric acid ;
(*c*) availability of corrosion resistant equipment ;
(*d*) demand within the country or outside.

So far as the proteinous materials are concerned, maize gluten is available in fairly sufficient quantities. At present there are two established starch factories, one in Lyallpur and the other in Peshawar with a capacity of about 12.5 and 24.5 tons of starch per day, respectively. These two factories are making

TABLE II

YIELDS OF GLUTAMIC ACID AND SODIUM GLUTAMATE BY VARIOUS METHODS

Proteinous material	Time	Sp. Gr. of acid	Per cent of glutamic acid hydrochloride	Per cent of glutamic acid	Per cent of sodium glutamate
Wheat gluten					
(1) ..	18 hours	1.18	14.0	9.0	11.5
(2) ..	6 „	1.18	23.2	15.2	19 0
(3) ..	6 „	1.03	——	14.5	17.6
(4) ..	9 „	1.03	21.65	——	18.38
Maize gluten					
(1) ..	9 „	1.03	10.4	6.8	7.4
(2) ..	12 „	1.14	15.9	10.3	13.0
Casein ..	24 „	1.14	18.1	11.5	14.3

their starch from maize. Besides these two factories, there are some smaller concerns making their starch from wheat. Their production, no doubt, is smaller but still they are producing a good amount of gluten. This gluten whether from maize starch or from the wheat starch is finding particularly no remunerative application. It is mainly used as a cattle feed. If it could be converted into glutamic acid, this by-product can yield better dividends. In addition to these two sources of gluten, Pakistan has also abundant supply of cotton-seed oil cakes which contain a good amount of gluten. This source can also be utilized for the production of glutamic acid.

Hydrochloric acid can, no doubt, be manufactured from sulphuric acid and sodium chloride. The capacity for the production of sulphuric acid in the country is much more than its consumption at present. The excess of sulphuric acid can be utilized in the production of hydrochloric acid. Hydrochloric acid is also now obtained as a by-product from the manufacture of D.D.T. and also from the caustic soda plant at Nowshera by electrolytic process through the production of hydrogen and chlorine.

Regarding corrosion resistant equipment, the country has to import it from abroad. Such equipment can be fabricated either from stainless steel containing molybdenum or it can be glass-lined or rubber-lined. Nowadays synthetic resins are also used for lining such equipment in order to withstand the action of concentrated hydrochloric acid.

Monosodium salt of glutamic acid, as is well-known, gives that peculiar meaty odour and flavour to the food which would be very popular among the meat-eating population of Pakistan. This material can be introduced in the beginning, in military rations, in restaurants etc. and when the general public gets sampled with it they would naturally go in for its consumption. If it could be made economically within the country, there will be a likelihood of an export market for it to countries *viz*. China, Japan and America where it has a fairly high record of consumption.

References

1. J. Sci. Ind. Res. (India) **13 B**, 222 (1954).
2. Sorks, U.S. Patent (1953) 2,631,952.
3. H.J. Ritthausen, Prakt. Chem. (1866) 99.
4. Symposium on monosodium glutamate, Chicago, 5, March 1948.
5. K. Ikeda, "Original Communications Eighth International Congress of Applied Chemistry" **18**,147 (1912).
6. Morris B. Jacobs, Food and Food Products, **1**,618 (1944).
7. Edgar A. Ferguson, Jr., U.S. Patent (March 1953) 2,631,119.
8. Morris B. Jacobs, Food and Food Products, **II**, 497, (1944).
9. Forrest A. Hoglan, U.S. Patent, (March 8, 1949.) 2,463,877.

EVALUATION OF FUNGICIDAL PROPERTIES OF LIGNIN ACETIC ACID

Part I—Studies on Fungus Organisms in Petri-plates

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DURING the investigation on utilization of lignin from paper mills' waste (black liquor), we were able to synthesise lignin acetic acid which had been said[1] to have fungicidal and insecticidal properties. Our attention was drawn to the fungal diseases of jute plants which is one of the main agricultural crops of East Pakistan. The fungal diseases sometimes cause havoc to the plants in some places, even about 60.0% damage of the crops has so far been reported[2] and this was gradually becoming a headache to the growers.

The following parasitic fungi of jute plants were included in the present study : (a) *Rhizoctonia sp.*—a soil-borne pathogen causing wilting of jute plants in older age and damping off in seedling period ; (b) *Colletotrichum corchori*—a seed-borne pathogen of jute plants causing anthracnose of jute seedlings ultimately killing the affected plants ; (c) *Macrophomina phaseoli* and (d) *Diplodia corchori* (*Botryo-diplodia*)—organisms causing stem rot and black band diseases to jute plants. Along with the jute pathogens *Memoniella echinata*, a highly cellulose destroying organism isolated from mildewed cotton, was also used to find out the fungicidal properties of the above chemical against it.

Considering the above facts, preliminary sets of experiments were arranged with the above mentioned organisms in petri plates. Experiments conducted with lignin acetic acid included (i) the effect upon the growth of the fungus organism in the laboratory medium (ii) the effect of the treatment on jute seeds and (iii) the effect of treating cotton threads against *Memnoniella*.

Preparation of Medium: Czapeck's agar medium was used for the experiments in the petri-plates. The composition of the medium used was as follows :—

Glucose	..	..	1.00%
Peptone	..	..	0.50%
KH_2PO_4	..	..	0.20%
$MgSO_4$	..	..	0.50%
Agar	..	..	2.00%

Thus the prepared medium was found to be most suitable one and used in petri-plate experiments.

Toxic Effect

Some experiments were carried out with the sample of lignin acetic acid* sprayed on the surface of 15 ml. sterilized medium in the petri-plate and the respective organisms cultured at the centre to see the growth of the fungus. Some peculiar behaviour has been observed. In some cases the fungus grew outwards uniformly, in some cases there were quite irregular growth and others had very thin layer. These irregularities and lesser growth of fungus compared to the control was a clear indication of toxic effect of lignin acetic acid upon some fungi. The results of a particular case of *Rhizactonia sp.* tried in this manner are shown in Table I.

Modified Procedure

In view of the above results, the work of quantitative evaluation of fungicidal properties of lignin acetic acid was undertaken and the experimental procedure was modified to some extent in the light of previous observation. Lignin acetic acid was quite soluble in ethanol. In 10 ml. ethanol 1.0 g. of the substance could be dissolved and when added to 100 ml. portion of the above mentioned Czapeck's medium, it was found to remain fairly in solution. Different concentrations (*e.g.*, 0.25%, 0.5% and 1.0% etc.) of the substance were prepared in the medium along with the blank Czapeck's medium in a medium in a separate flask for control experiment. These media were sterilized under 15 lb. pressure for 15 minutes. After proper sterilization the media were plated in petri-plates, 15 ml. in each plate. The test organisms were cultured at one edge of the dishes so that the linear growth after each 24 hours could conveniently be measured (radius in mm.) The results were always compared with the control experiments. Moreover, lignin acetic acid was also compared with a standard fungicide Nomersan (I.C.I. product) as available in the market.

*Lignin acetic acid found insoluble in water.

Table I

Extent of Inhibition of the Growth of Fungus Organism

Organism inoculated—*Rhizoctonia sp.*

Lignin acetic acid samples*	Concn. of the sample in 15 ml. medium (%)	Diameter of the ring in cm.	Mean (cm.)	Difference of diameters of the control and test expt. in cm.	Percentage of inhibition† (%)
Sample I ..	0.5	5.5 5.7	5.6	0.8	12.5
	1.0	5.0 4.8	4.9	1.5	23.4
Sample II ..	0.5	5.6 5.8	5.7	0.7	10.9
	1.0	5.1 4.9	5.0	1.4	21.8
Control ..	nil	6.4	6.4	—	—

*Sample I and II were prepared in aqueous and acid medium respectively.

†Calculation :—

$$\text{Percentage of inhibition} = \frac{D_x}{D_c} \times 100$$

where D_x, the difference of diameters of the control and test experiment and D_c, the diameter of the control experiment.

The aforesaid fungus organisms were studied elaborately under modified conditions with different concentrations of lignin acetic acid so as to ascertain the minimum percentage required to check the growth of the test organisms. Concentrations varied between 0.25—5.0% of lignin acetic acid and the organisms were allowed to grow upto 240 hours in some cases. Results are tabulated in Tables II-VI below.

A graphical representation of the above results is shown in figure I. In the case of *Rhizoctonia* and *Colletotrichum* the effect is very pronounced and in the case of *Macrophomina* and *Botryodiplodia* too there are some definite effects. A very interesting phenomenon was observed with regard to the rate of growth of the test organisms. Almost in all cases the growth of the fungi was checked considerably at the initial stages but after certain period of time the growth was quite rapid. The inhibiting power of lignin acetic acid was found diminished with the time which might be due to some pathogenic decomposition of the acid in the medium. This may throw some light on the utilization of lignin acetic acid. This point has not yet been ascertained.

In view of the results in table VI, lignin acetic acid was tried to use as a controlling agent for *Memononiella* causing damage to the textile goods. One experiment with cotton thread was carried out under favourable conditions. The cotton thread was sprayed with 0.1% lignin acetic acid with spore suspension in the solution and kept in a saturated humid chamber. A similar suspension of spores in distilled water was also sprayed in another set of cotton thread under identical conditions for control. A profuse growth of the organism was noticed on the control set after two to three weeks whereas a feeble growth observed on the other set. It was considered a higher concentration might give better results as seen in the petri-plate experiments (*vide* Table VI). Some of the experiments were also done with different concentrations of lignin acetic acid.

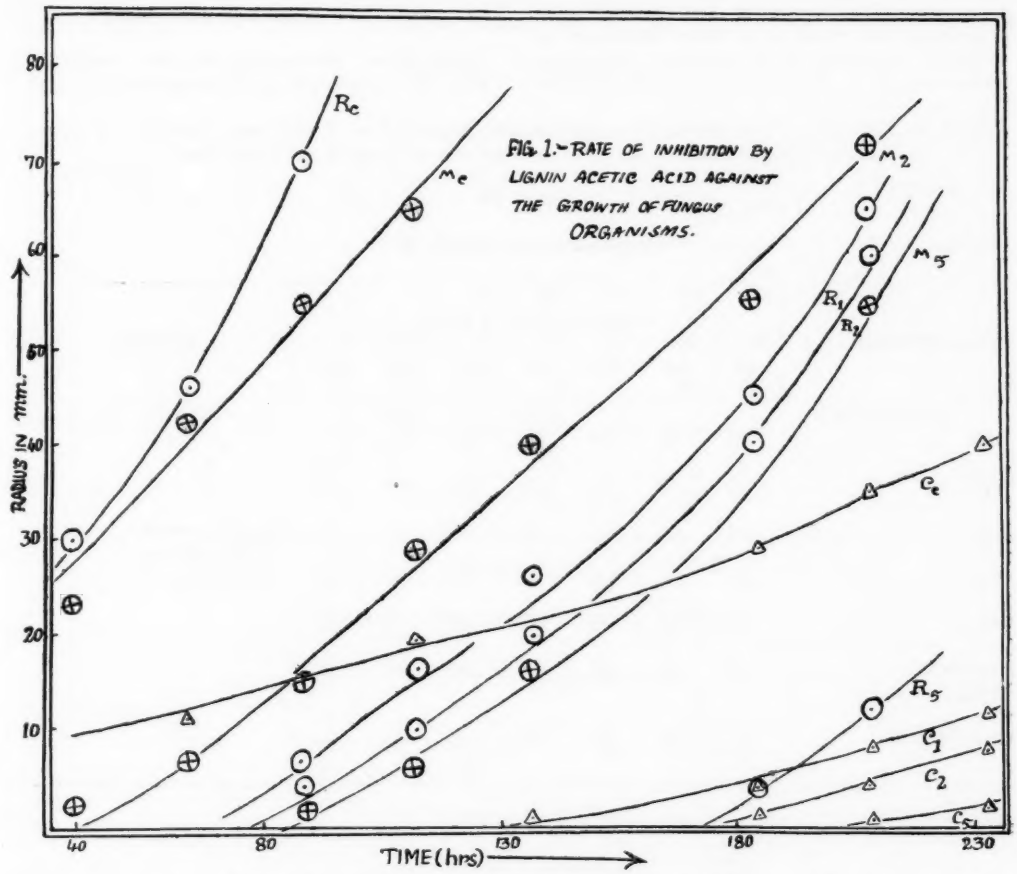

Fig. 1.—Rate of inhibition by lignin acetic acid against the growth of fungus organisms.

—⊙— for Rhizoctonia sq. (vide Table II).

R1	,,	,,	against 1.0 % lignin acetic acid.
R2	,,	,,	,, 2.0 % ,,
R5	,,	,,	,, 5.0 % ,,
Rc	,,	,,	control

—△— for Colletotrichum (Vide Table III).

C1	,,	,,	against 1.0 % lignin acetic acid.
C2	,,	,,	,, 2.0 % ,,
C5	,,	,,	,, 5.0 % ,,
Cc	,,	,,	control

—⊕— for Macrophomina (Vide Table IV).

M2	,,	,,	against 2.0 % lignin acetic acid.
M5	,,	,,	,, 5.0 % ,,
Mc	,,	,,	control

As a controlling agent the acid proved quite promising but there is a little handicap in using this material for it imparts a somewhat brown colour to the cotton and hence further investigation in this line was abandoned.

From close observation of the results in Table II-V it was clearly indicated that the acid

Effect of Different Concentrations of Lignin Acetic Acid Upon the Growth of Fungi (Radius Measured in mm.) for a Different Length of Time Hrs.)

Table II

Organisam—*Rhizoctonia sp.*

Concentrations (%)	Length of time in hours							Remarks
	40	64	88	112	136	184	208	
0.25 ..	8	18	30	45	60	over 70	—	
0.50 ..	5	15	25	40	53	70	over 70	
1.00 ..	nil	nil	6.5	16	26	45	65	Rapid growth with uniform inhibition.
2.00 ..	nil	nil	4.5	10	20	40	60	
5.00 ..	nil	nil	nil	nil	nil	4	12	
Nomersan (0.6%) ..	nil	nil	nil	nil	nil	nil	nil	
Control ..	30	46	70	80	over 90	—	—	

Table III

Organism—*Collectotrichum*

Concentration (%)	Length of time in hours								Remarks
	40	64	88	112	136	184	208	232	
0.25 ..	nil	nil	2	5	9	15	20	25	
0.5 ..	nil	nil	nil	1	3	6	10	14	
1.0 ..	nil	nil	nil	nil	1	4	8	11	Normal
2.0 ..	nil	nil	nil	nil	nil	1	4	8	
5.0 ..	nil	nil	nil	nil	nil	nil	0.5	2	
Nomersan (0.6%)	nil	nil	nil	nil	nil	nil	nil	nil	
Control ..	6	10.5	15	20	25	29	35	40	

TABLE IV

Organism—*Macrophomina*

Concentration (%)	Length of time in hours							Remarks
	40	64	88	112	136	184	208	
1.0 ..	3	12	25	41	58	75	over 80	Rapid growth
2.0 ..	2	6.5	15	29	40	55	72	
5.0 ..	nil	nil	2	5	16	30	55	
Nomersan (0.6%) ..	nil	nil	nil	nil	nil	nil	nil	
Control ..	23	42	55	65	78	over 80	—	

TABLE V

Organism—*Botryodiplodia* (*Diplodia corchori*)

Concentration (%)	Length of time in hours				Remarks
	48	72	120	144	
1.0 ..	20	58	over 80	—	Irregular growth
2.0 ..	15	48	75	over 80	
5.0 ..	10	35	65	80	
Nomersan (0.6%) ..	nil	nil	nil	nil	
Control ..	29	75	over 80	—	

might have its use as a controlling agent for diseases of jute plants. Elaborate studies of this possibility have subsequently been made with jute seedlings and will be published later.

For the suitable utilization of lignin acetic acid, its fungicidal properties were studied on a quantitative basis against five pathogens *viz. Rhizactonia sp.*, *Collectotrichum*, *Macrophomina*, *Botryodiplodia* and *Memnoniella*. The experiments were carried out in the petri-plates in Czapeck's agar medium. Lignin acetic acid was proved a promising controlling agent against the above fungi especially *Rhizoctonia sp.* and *Collectotrichum*. A graphcial repretation of the above results is also given.

Acknowledgement

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A part of the work was done in the Mycology Section of the Department of Botany and our

TABLE VI

Organism—*Memnoniella*

Concentration (%)	Length of time in hours							Remarks
	48	72	120	168	192	216	240	
0.25 ..	nil	nil	nil	nil	1	2.5	5	
0.5 ..	nil	nil	nil	nil	nil	1	3	
1.0 ..	nil	nil	nil	nil	nil	nil	1	Very slow growth.
Nomersan (0.6%) ..	nil	nil	nil	nil	nil	nil	nil	
Control ..	1	2	3	4	5	7	9	

thanks are due to Prof. M. Ahmad for the courtesy.

Our thanks are also due to Karnaphuli Paper Mills Ltd. for the supply of the black liquor.

References

1. Device U.S.P. 2,503, 297.
2. K.M. Badruddoza, Krishi-Katha **14**, No. 2, 120, (1954).

PESTICIDAL ACTION OF MAKEROL, SHARIGOL AND JHIMPIROL

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IN a process worked out by Siddiqui et al., [1,2] for the desulphurisation of coal and the simultaneous recovery of depolymerised coal resin through the superheated steam treatment of pulverised coal at sub-carbonization temperatures, steam volatile sulphur containing liquids were obtained as by-products. These liquids which have been provisionally named as Makerol, Sharigol and Jhimpirol according to the places of origin of coals, have a sulphur content of about three per cent and a distillation range corresponding to that of terpenes and sesqueterpenes.

The isolation, chemical composition and constitution of the various fractions constituting these liquids are being carried out in the Chemical Division of the Central Laboratories.

On the suggestion of S. Siddiqui, to study the pesticidal properties of these products, preliminary work was carried out on their insecticidal action under a scheme financed by the Pakistan Council of Scientific and Industrial Research, at the Department of Zoology, University of Karachi, Siddiqui et al., [3,4] Ashrafi.[5]

The present paper deals with studies carried out in this direction at the Central Laboratories, initially with the object of finding out :

1. the immediate knock down effect of sprays ;
2. the effect of oral feeding, application on cuticle and injection into the body cavity of insects ;

3. the fumigant action on stored grain pests;
4. the effect of vapours of these liquids on flying insects like houseflies and mosquitoes ;
5. the repellent action on anopheline mosquitoes and houseflies ;
6. the synergistic action of Makerol and Sharigol on insecticides in common use ;
7. the effect on the germination of seeds after fumigation and soaking in Makerol and Sharigol.

For testing the immediate knock down effect, five to ten per cent solutions of Makerol and Sharigol in kerosene and in water with Teepol [sodium secondary alkyl (C10-C18) sulphate] as emulgant were used.

The results were compared with a solution of Pyretherum in kerosene corresponding to 0·1% content of pyretherins.

Evaluation of Toxicity

To evaluate the toxicity of Sharigol by oral feeding in cockroaches (*Periplaneta americana*), they were allowed to lick desired amounts of Sharigol through a syringe needle and were then kept under observation for 24 hours. Table I summarizes the results obtained.

The values when plotted cumulatively on a dosage mortality graph give an asymmetrical sigmoid curve. In order to calculate LD_{50} from these data the mortality percentages have been transformed into probability units and then plotted against log dosage, Bliss, 6,7 figure I.

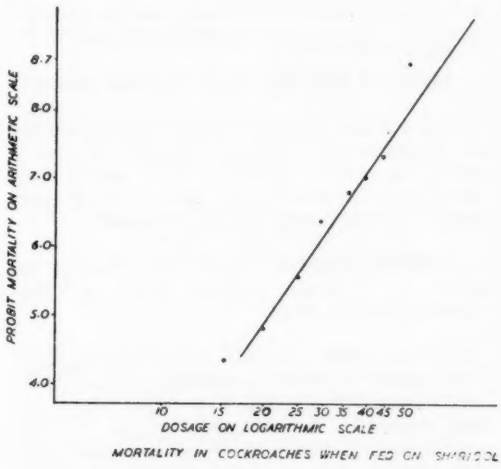

Fig. 1.

Sharigol was also applied on the tarsi cuticle and the neck of cockroaches *P. americana*. When 50 mg. per kg. of the body weight of Sharigol was applied to cockroach integument, death occurred within 24 hours.

Five per cent aqueous emulsion of Sharigol was also injected by means of a microsyringe in the body cavity of cockroaches. Table II below summarizes the results.

TABLE I

TOXICITY OF SHARIGOL TO COCKROACHES BY ORAL FEEDING

Concentration mg./Kg. of body weight	Percent mortality in 24 hours	LD_{50}	LD_{90}
15	27		
20	45	20.1	
25	68		
30	91		
35	95		
40	98		30
45	98		
50	100		

TABLE II

SHOWING THE TOXICITY OF SHARIGOL TO COCKROACHES BY INJECTION

mg./kg. of body weight of Sharigol injected	Percent mortality in 24 hours.	LD_{50}	LD_{90}
5	30		
6	38		
7	52	6.2	
8	83		
9	92		
10	98		
11	98		8.8
12	99		

Controls were run with all the above experiments and the results have been corrected for deaths in controls using Abbott's formula $\frac{(x-y)}{x} \times 100$, where x is the per cent survival in the untreated control, and y is the per cent survival in the treated experimental sample. [8]

Makerol and Sharigol as Fumigants

Makerol and Sharigol appear to be promising as fumigants and therefore a series of experiments have been carried out to assess their effectiveness in this respect, against stored grain pests. The following insects were used :

1. *Calandra oryzae* adult ; 2. *Bruchus sp.* adult ; 3. *Tribolium castaneum* adult ; 4. *Rhizopertha dominica* adult.

Glass containers of one to 20 litre capacity were taken. In these containers 50 laboratory bred adults between five to eight days old were released. A green filter paper No. 405 was hung in the middle of the container. By means of a microsyringe a measured quantity of the fumigant was dropped on the paper. The container was then tightly corked and kept closed for a desired length of time, after which the insects were transferred to fresh containers and observed for 24 hours.

After some experimentation, concentrations were selected to determine the ranges of mortality at high to low levels of concentration. Several replications at one concentration were done and their mean taken. Table III below gives the mean values at each concentration for the replicates.

The values with respect to *Calandra Oryzae* in Table III are plotted cumulatively on a dosage mortality graph, fig. 2. The resulting curves in the case of carbon bisulphide and Sharigol are more or less typical of fumigants but the curve of Makerol tends to become very much asymmetrical as the percentage kill exceeds 85 per cent. This shows that a very high dose of Makerol is required to obtain kills of more than 85 per cent.

In figure 3 the above curves have been transformed into straight lines by transforming percentages into probability units, probits, and then plotting them against log dosages, Bliss.[7] LD_{50} and LD_{90} have been calculated from figure 3.

From figure 3 it would be seen that in lower dosages, both Makerol and Sharigol are

TABLE III

FUMIGATION OF STORED GRAIN PESTS

Fumigant	Insect	Concentration of the fumigant in parts per million	Percent Mortality in 24 hours	LD_{50}	LD_{90}
Sharigol (a)	*Calandra oryzae*	4	42	5·7	
		7	52		
		8	67		
		10	85		
		12	92		
		13	97		
		14	98	9·7	
		16	99		
		17	100		
Makerol	*Calandra oryzae*	4	40		
		7	48	7.6	
		8	58		
		10	74		
		11	82		
		12	85		
		14	88		
		16	90		13·3
Makerol (a)		20	95		
		24	100		
Carbon-bisulphide	*Calandra oryzae*	4	0		
		6	38		
		8	44		

TABLE III—contd.

Fumigant	Insect	Concentration of the fumigant in parts per million	Percent Mortality in 24 hours	LD_{50}	LD_{90}
		10	80	7.9	11.8
		12	95		
		14	99		
		16	100		
Sharigol (b)	*B.phaseoli*	4	25		
		6	37		
		7	60	5.5	7.4
		8	95		
		11	00		
Makerol	*B.phaseoli*	8	16		
		12	84		
		16	90	10.3	17.8
		24	94		
		32	98		
		40	100		
Carbon-bisulphide (b)	*B.phaseoli*	8	4		
		12	50		
		14	96	10.7	12.7
		16	100		

superior to carbon bisulphide. LD_{50} for Sharigol is 5.7 parts per million, for Makerol 7.6 p.p.m. for CS_2 7.9 p.p.m. At a dose of about 9.3 p.p.m. Makerol and carbon-bisulphide are equally effective giving about 65 per cent kill. At higher doses, however, Makerol becomes less effective. Upto a dose of 11 p.p.m. Sharigol is more effective than carbon bisulphide at 11 p.p.m. ; both are equally effective giving a mortality of about 88 per cent, but at higher doses carbon bisulphide excels Sharigol. LD_{90} for the three fumigants are as follows :—

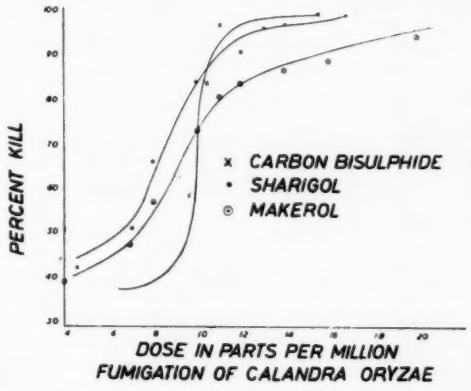

Fig. 2

Makerol ..	.. 13.3 p.p.m.
Sharigol ..	.. 9.7
Carbon bisulphide	.. 11.8

Giving better kill at lower dosage is a desirable feature of Sharigol and Makerol, and, used in conjunction with other fumigants, they might, on further work which is in progress, prove very valuable.

Results with *Tribolium castaneum* and *Rhizopertha dominica* were similar to those obtained with *Calandra oryzae*.

Experiments on the amount of fumigant absorbed by grains and on fumigation of infested grains are underway and will be reported in a separate paper.

The toxicity of the vapours of Makerol and Sharigol to flying insects like houseflies and mosquitoes was also tested to explore the possibility of their utilization in the shape of insecticide joss sticks and for controlling insects in enclosed spaces or in places like thick bushes etc., where it is impossible to obtain immediate control through the use of contact insecticides. A field where this may be effective would be

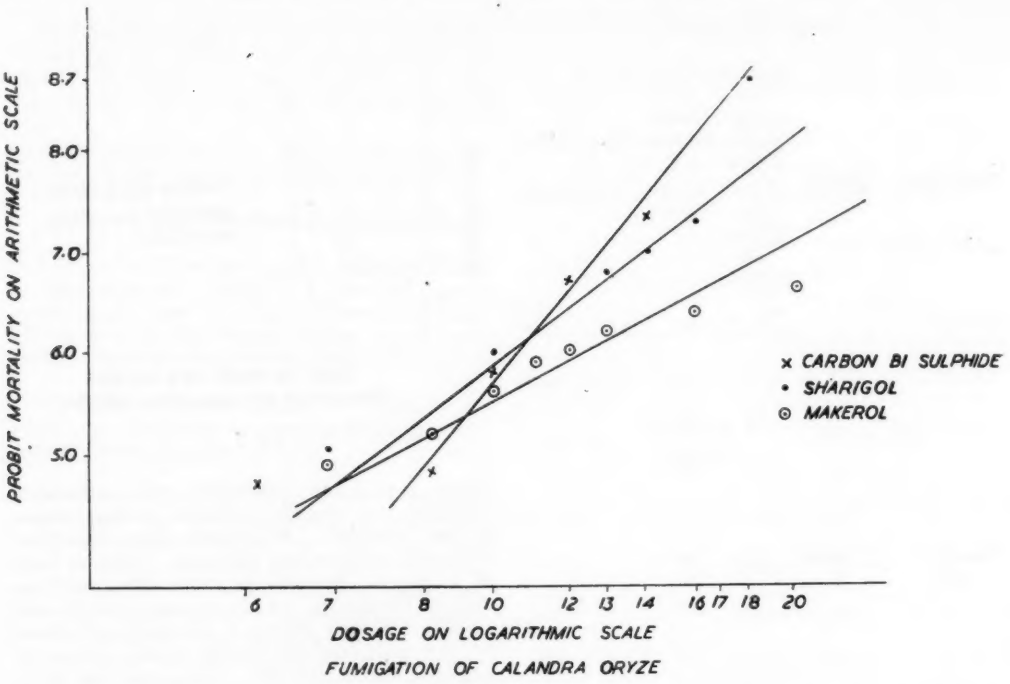

Fig. 3.

the control of Tsetse flies in Africa. For their control Buxton[9] has recommended DDT "smoke". Sharigol and Makerol used in conjunction with DDT "Smoke" will have the added advantage of deep penetration and give immediate knock down.

Sharigol and Makerol by virtue of being fumigants as well as contact poisons and being almost non-toxic to man will also fine a good use in the immediate control of cockroaches, bed bugs, fleas etc. in houses.

To test the knock down action of these vapours laboratory reared house flies (*Musca domestica*) 3 days old were exposed to vapours in enclosed spaces of 10 and 20 litres. An arbitrary effective limit of 100% knock down in 20 minutes time with not more than one per cent revival in 24 hours was chosen and different concentrations which gave 100% knock down in less than 20 minutes with not more than one per cent revival were tried and the times of first and subsequent knock downs were noted. After an exposure of 10 or 20 minutes as given in table IV flies were removed to a fresh cage and were kept under observation for 24 hours. Revivals, if any, were noted. Several replicates were done and the mean for each knock down was taken. Table IV summarizes the results of the first 50% and the last knock down as well as revivals at different concentrations.

Figures 4 a, b and c also show percentage mortality at different exposure times in minutes plotted on a probit log time scale taking probit as an independent variable.

A comparison has also been made of the relative knock down properties of Makerol and Sharigol at median effective time *i.e.*, the time required for 50% knock down. Table V below gives the relative effectiveness :—

TABLE V

SHOWING COMPARATIVE EFFECTIVENESS OF MAKEROL AND SHARIGOL AT DIFFERENT CONCENTRATIONS

Concentration in parts per million	Insecticide	Median effective time (time of 50% K.D.)	Makerol/ Sharigol
16	Makerol	18.3	1.25
	Sharigol	14.6	
32	Makerol	8.5	1.32
	Sharigol		
48	Makerol	5.6	2
	Sharigol	2.8	

TABLE IV

SHOWING FIRST MEDIAN AND LAST KNOCK DOWN TIMES AT DIFFERENT CONCENTRATIONS OF MAKEROL AND SHARIGOL

Insecticide	Concentration in parts per million	1st K.D. time	Median K.D. time	Last K.D. time	Exposure time in minutes	Revival percentage
Sharigol	16	7.83	14.6	16.66	20	nil.
,,	32	3.71	6.5	8.78	10	—do—
	48	1.59	2.8	5.29	10	—do—
Makerol	16	8.45	18.3	19.80	20	0.01
	32	4.61	8.5	10.44	10	nil.
	48	2.83	5.6	8.73	10	—do—

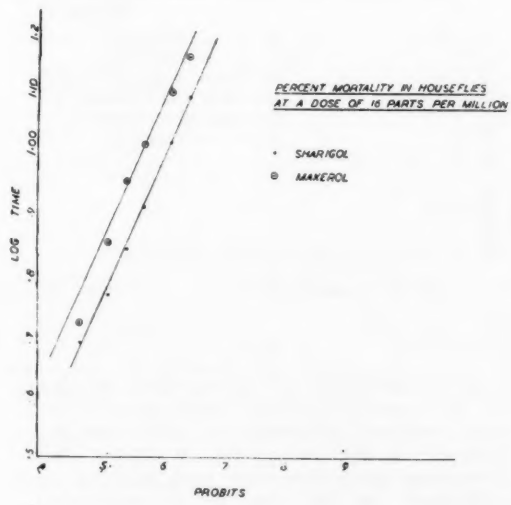

Fig. 4 (a).

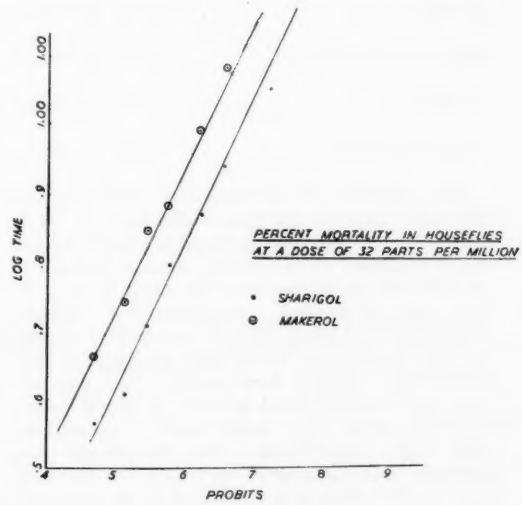

Fig. 4 (b).

At all the levels Sharigol gives quicker median effective (50%) knock down time than Makerol. At lower concentration *i.e.*, at 16 p.p.m. the difference is small *i.e.*, of the order of 125:100 but as the dose increases Sharigol becomes relatively more and more effective. At 48 p.p.m. Sharigol is twice as effective as Makerol.

Insect Repellence

Sharigol and Jhimpirol are good anopheline repellents. Experiments were conducted with *Anopheles stephensi*, the vector of malaria in Karachi.

The technique used was a modification of

that developed by Granett (1940)[10] and Morton et al.[11]

Two-tenth ml. of the substance under trial was distributed evenly over a hand and part of a forearm which were then exposed to about 1,000 female mosquitoes, *A. stephensi*, in a one ft. cube cage for 10 minutes at 30 minutes intervals. The time between the application and first bite was taken as the maximum effective repellent time.

The following repellents were used in the comparative study : oil of citronella, dimethyl phthalate, Makerol, Sharigol, Jhimpirol and a commercial liquid repellent. Table VI below summarises the results.

TABLE VI.—SHOWING THE PROTECTION TIME OF DIFFERENT REPELLENTS

Repellent	*Protection time*
Dimethyl phthalate ..	3 hr. 11 min.
Sharigol	2 hr. 48 min.
Jhimpirol	2 hr. 42 min.
Commercial repellent ..	2 hr. 32 min.
Makerol	1 hr. 23 min.
Oil of citronella	0 hr. 44 min.

As a further test of mosquito repellence the following experiment was conducted. A hand and part of an arm, treated with 0.2 ml. of the compound to be tested, were exposed for 10 minutes at 30 minutes intervals in a 1 ft. cube cage containing 1,000 hungry *A. stephensi* mosquitoes. The number of mosquitoes alighting on the treated hand and arm during the ten minute period was noted. The mosquitoes were not allowed to take a blood meal. Controls were run under similar conditions with each experiment. The percentage repellence was calculated by using the formula $\frac{(x-y)}{x} \times 100$ where x is the number of mosquitoes alighting on the hand in a ten-minute period in the control, y the number of mosquitoes alighting on the hand in the experiment.

The same compounds were used in this experiment as in the previous one. Table VII below summarises the results :

Figure 5 expresses these results on a graph for easy comparison.

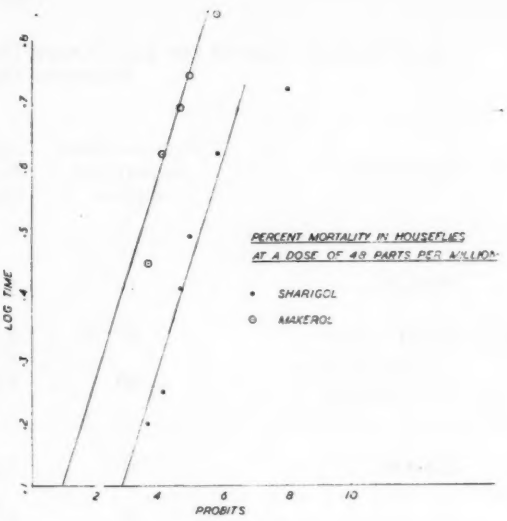

Fig. 4 (c)

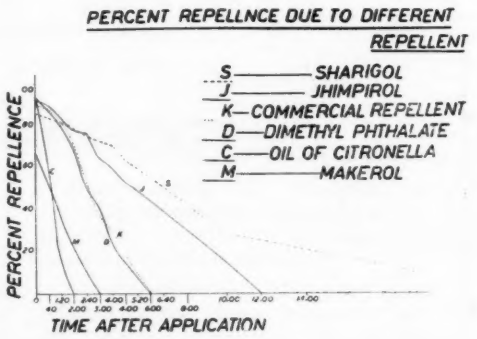

Fig. 5

After application of the repellent, as given in the experiment above, hands were washed with ordinary toilet soap and water and then exposed to the mosquitoes as above. The percentage protection after each washing was calculated as in the above experiment. Table VIII summarizes the results obtained.

There is also some experimental evidence to show that Sharigol has a slight a mild synergistic action on some known insecticides. The results of the work in this direction will be reported in a separate paper.

The effect of fumigation and soaking of seeds in Makerol and Sharigol was also studied. Mung (*Phaseolus mungs*) seeds were chosen for

TABLE VII

SHOWING PERCENT REPELLENCE DUE TO DIFFERENT REPELLENTS

Time in hours after application	Sharigol	Jhimpirol	Commercial repellent	Dimethyl phthalate	Makerol	Oil of citronella
Immediately after application	86	93	90	93	68	93
0 hr. 40 min.	84	90	89	88	52	64
1 hr. 20 min.	82	84	83	82	35	16
2 hr. 0 min.	79	78	70	70	23	0
2 hr. 40 min.	75	77	55	53	11	
3 hr. 20 min.	73	65	38	42	0	
4 hr. 0 min.	71	60	30	20		
4 hr. 40 min.	64	53	19	11		
5 hr. 2 min.	50	49	0	0		
6 hr. 0 min.	48	48				
10 hr. 0 min.	29	27				
18 hr.	15					

TABLE VIII

SHOWING PERCENT REPELLENCE AFTER WASHING WITH SOAP AND WATER

	After one washing with soap and water	After two washings with soap and water
Jhimpirol	63	35
Sharigol	58	29
Commercial repellent	55	21
Oil of citronella	42	10
Makerol	31	10
Dimethyl phthalate	10	0

the experiment. These seeds were fumigated with high doses of Makerol and Sharigol for 24 to 48 hours. They were also soaked in Makerol and Sharigol for 24 to 96 hours. Each lot of the fumigated and soaked seeds after treatment was divided into two equal batches, one was kept for germination between moist cotton pads immediately, and the other was

allowed to desorb for 24 hours and then kept for germination. Controls were run with each batch. The results obtained show that fumigation of seeds by Makerol and Sharigol has a beneficial effect on germination. With the increase in fumigation dose there is an increase in percentage of germination of seeds.

Soaking of seeds in Makerol or Sharigol also does not seem to harm the seeds much, if the seeds are allowed to desorb for 24 hours after soaking. But if the seeds are not allowed to desorb and kept for germination immediately, germination is greatly hampered.

The higher percentage of germination among fumigated seeds is probably due to the killing of fungus spores. On the basis of preliminary studies in the fungicidal properties of Makerol and Sharigol, it appears that these products have a marked fungicidal action.

Acknowledgements

The authors are grateful to Dr. S. Siddiqui for his direction and valuable suggestions through the progress of this work. The authors wish to thank Dr. Shujat-ul-Akbar and Mr. N. H. Naqvi who were associated with this work during its earlier stages. The authors also tender their thanks to Mr. Sadiq Husain and Mr. M.S. Anwar of the Department of Plant Protection and to Dr. Maqsood Nasir of the Ministry of Food for making some stored grain pests available for starting cultures for our tests.

References

1. S. Siddiqui, Pakistan Patent No. 105108, March 26, 1953.
2. S. Siddiqui, and M.N. Ahmed, Pakistan Patent No. 105109, April 4, 1953.
3. S. Siddiqui, and S. A. Warsi, Abstracts Section of Chemistry (applied chemistry), Pakistan Association for the Advancement of Science, p. 52 (1954).
4. S. Siddiqui, S.A. Warsi and S.A. Ahmed, Abstracts, Section of Chemistry : Applied Chemistry, Pakistan Association for the Advancement of Science, p. 35 (1955).
5. S.H. Ashrafi, Abstracts, Section of Chemistry : Applied Chemistry, Pakistan Association for the Advancement of Science, p. 28 (1955).
6. C.I. Bliss, Science **97,** 38-39 (1935).
7. C.I., Bliss, Ann. Appl-Biol, 22, 134-167 (1935).
8. Abbot. 1925. From Insect Control by Chemicals, A.W.A. Brown (John Wiley and Sons, p. 764.
9. P.A. Buxton, Proc. 4th Internat. Cong. Trop. Med. and Malaria, Washington D.C. (Abstracts) (1948).
10. P. Granett, Journ. Econ. Ent. **33,** 563-565 (1940).
11. F.A. Morton, B.V. Travis and J.P. Linduska, U.S. Department of Agriculture. Bulletin No. E. 733 (1947).

PRELIMINARY STUDIES ON THE FUNGICIDAL PROPERTIES OF MAKEROL AND SHARIGOL

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IN the course of experiments on the effect of fumigation with Makerol and Sharigol on the germination of seeds it was observed that fumigated seeds gave a significantly higher percentage of germination. This was considered to be possibly due to the fungicidal action of Makerol and Sharigol, and preliminary studies carried out in this direction appear to support this view.

Aspergillus niger and *Alternaria sp.* have been used in this work as test fungi. Two series of tests were performed. In one of them the substance to be tested was mixed with potato dextrose agar medium in varying proportions of 1:1200, 1:600 and 1:400 ; the medium was poured in petri dishes A, B and C respectively, and the petri dishes were then inoculated with spores of the fungus. After inoculation the dishes were kept at room temperature which varied during experimentation from 25°C. to 27°C. Several replicates were done and controls were run with each set of replicates.

Tests with Aspergillus niger

After 24 hours of inoculation in the control, there was considerable growth of mycelium. But in the treated petri dishes there was no growth.

After 48 hours there was a luxuriant growth in the controls and spore formation started. In the experimental petri dish A, treated in the ratio of 1:1200 there was an abnormal stunted and very slight growth of mycelium, Plate I, petri dish A. When studied under microscope the mycelium appeared very closely interwoven and meshed presenting a thick mat-like appearance which thinned out at the edges. A bright yellow pigment also appeared in the mycelium. Petri dishes B and C treated in the ratios of 1:600 and 1:400 showed no growth. Plate II is a microphotograph of the teased mycelium from petri dish A.

Plate I is a photograph of the petri dishes A, B and C and control after 48 hours.

After 72 hours the controls showed a luxuriant growth and the fungus spread all over the medium. In petri dish A there was a further though very slight growth of the mycelium.

Aspergillus niger

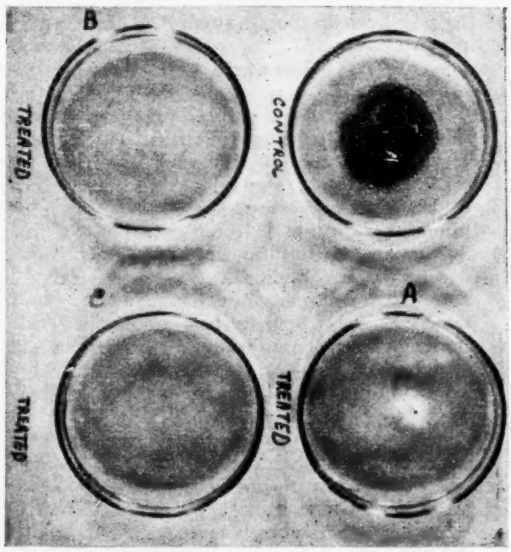


Plate No. 1 *48 Hours growth*

A Sharigol added to the medium in the ratio of 1 : 1200
B Sharigol added to the medium in the ratio of 1 : 600
C Sharigol added to the medium in the ratio of 1 : 400

Aspergillus niger

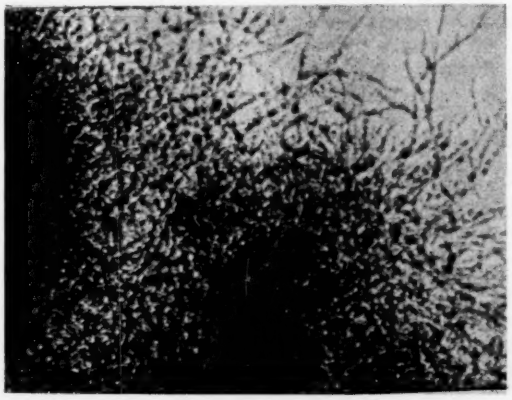


Plate No. II Microphotograph showing abnormal meshed and stunted growth of the mycelium.

There was, however, no spore formation and the yellow pigment became intense yellow. In petri dish B there was a very slight growth of mycelium about the size of a pinhead. In dish C there was no growth.

After a week the growth in the controls progressed normally whereas the growth in dishes A and B stopped, without any spores having been formed. In dish C there was no growth.

Alternaria spp.

In this case also a similar change took place. The growth of the mycelium in petri dishes A and B was stunted and very abnormal presenting a closely meshed interwoven structure under the microscope as shown in microphotograph, plate III. After about 72 hours a portion of the mycelium in petri dish A turned brown giving a gross appearance of conidial formation, but actually no conidia were formed. Seventy-two hours growth is shown in control and in petri dish A in plate IV.

In another series of experiments glass beads were smeared with spores of *Alternaria spp.* and *Aspergillus niger*. Some of these treated beads were fumigated with Sharigol at 1,000 parts per million ; a second batch was soaked in Sharigol and the third kept as control. After treatment these beads were put on potato dextrose agar medium in petri dishes. The spores on the beads which were fumigated and soaked failed to germinate. In the control there was normal growth.

These experiments show that Sharigol and Makerol inhibit the germination of spores and growth of mycelium. In low concentrations they retard and in higher concentrations they completely check spore formation in the fungus.

Spontaneous development of bright yellow pigment has been occasionally reported in the case of *A. niger*, but the production of a yellow pigment under experimental conditions is of interest as there appears to be no earlier reference to this in literature. Further work on the fungicidal activity of these products is in progress.

Alternaria sp.

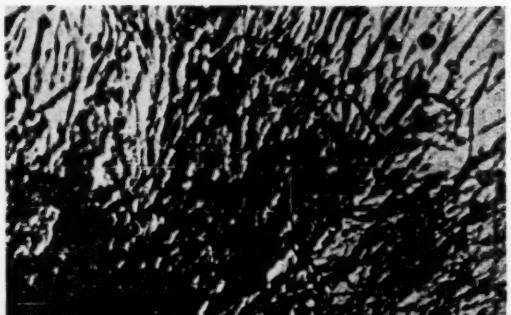


Plate No. III Microphotograph showing meshed and interwoven structure of the mycelium

Alternaria sp.

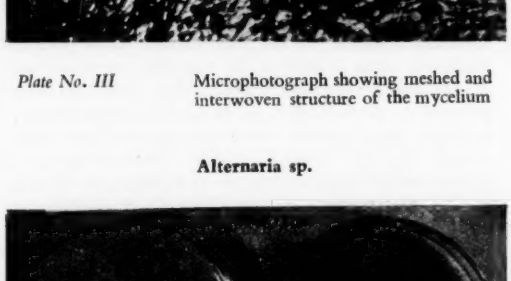


Plate No. IV *72 Hours growth*
A Makerol added to the medium in the ratio of 1 : 1200

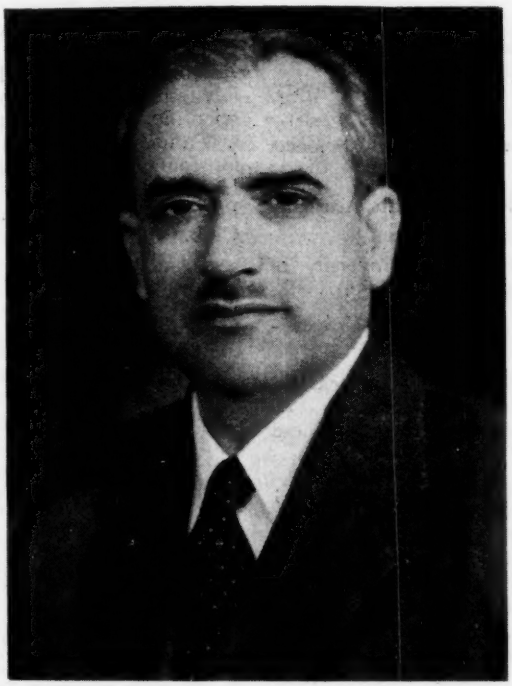
Acknowledgement

The authors acknowledge with thanks the help and valuable suggestions they received from Dr. Salimuzzaman Siddiqui ; thanks are also due to Dr. A.G. Kausar of the Department of Plant Protection for his help in supplying us cultures of fungi.

Obituary

DR. BASHIR AHMAD (1902 - 1957)

On the 14th of March, 1957, Pakistan suffered a grievous loss in the sudden passing away of an eminent biochemist, Dr. Bashir Ahmad. Since his return from China, where he led a delegation of Pakistani scientists in November last year, Dr. Bashir Ahmad occasionally suffered from shortness of breath. In February his complaint was diagnosed by a leading physician of Lahore as coronary insufficiency, and he was advised to take complete rest for three weeks in bed. With the heavy pressure of work from the side of the West Regional Laboratories as its Director, and the pressing responsibilities for the organisation of the Ninth Pakistan Science Conference at Peshawar, in his capacity as General Secretary of the Pakistan Association for the Advancement of Science, he made little of the medical warnings and did not allow himself the gravely needed rest. Persuasions to the contrary elicited only a promise of taking it easy for some time after the Science Conference. At 12 o'clock on the 14th of March, he delivered a lecture at the Food and Nutrition Symposium of the Science Conference on his life-long specialised field of work on carotenoids, and died of heart failure in his sleep the same afternoon. His body was brought to Lahore and laid to rest in the premises of the West Regional Laboratories.



Dr. Bashir Ahmad was born at Jullunder in 1902. After early schooling in his home town, he graduated from the Punjab University in 1923, securing first position in the University and winning several honours and a gold medal. He took his Ph.D. from the University College, London, in 1931. In 1933 he joined the All India Institute of Hygiene in Calcutta, where, as Assistant Professor and later Professor of Biochemistry and Nutrition, he carried out a series of investigations on various problems of fundamental importance in the field of biochemistry and nutrition. In 1941, he came back to the University of the Punjab as Professor of Organic Chemistry and Director, University Institute of Chemistry, where he continued till 1952, with a break of about three years (1944-47) when he worked as Assistant Director, National Chemical Laboratory, Poona, and was in charge of its planning in the Council of Scientific and Industrial Research (India). From 1952 to 1954, he was Vice-Chancellor of the Punjab University, and from 1954 until his death he was the Director of the West Regional Laboratories of the Council of Scientific and Industrial Research at Lahore.

Dr. Bashir Ahmad had extensively toured the U.K., the U.S.A., Canada, Australia and the continent of Europe, not only in connection with higher studies and research in specialised fields but also, under various travel grants, to acquaint himself with modern methods and techniques of scientific research. His researches in chemistry, biochemistry, nutrition, food and related subjects are covered by about 150 publications.

While the bibliography of his papers indicates the wide range of problems on which he worked, the level of his researches, conducted with

various collaborators, remained uniformly high. Dr. Bashir Ahmad chose the subject of nutrition for his speciality, and within this field, vitamins drew his major attention with special reference to vitamin A and the carotenoids. On the last subject he published no less than 23 original papers and some 7 review articles. Next in importance came vitamins B and C. Vitamin B_{12} is a cobalt compound, and it is significant that Dr. Bashir Ahmad was the first to tackle the problem of the cobalt content of the Punjab soils. There can be no better tribute to his memory than to carry on work in this field which was so dear to him.

Dr. Bashir Ahmad's scientific work brought him a host of distinctions. He was :

(*i*) Fellow, Royal Institute of Chemistry, London.

(*ii*) Fellow, National Institute of Sciences of India.

(*iii*) Foundation Fellow, Pakistan Academy of Sciences.

(*iv*) LL.D. (Honoris Causa), University of Cambridge, Great Britain (1953).

(*v*) Fellow, Punjab and Karachi Universities.

(*vi*) Member or Fellow of several learned societies ; President, Secretary or Treasurer of some of them. These include :

Indian Chemical Society, Calcutta ; Biochemical Society, London ; Society of Biochemistry and Experimental Medicine ; Society of Biological Chemists, India ; American Institute of Nutrition ; Indian Pharmaceutical Association ; Indian Science Congress ; Lahore Philosophical Society ; Indian Science News Association ; Biochemical Society, Calcutta ; Physiological Society of India ; National Nutrition Association of India ; Pakistan Associaiation for the Advancement of Science ; Royal Society of Arts, London.

(*vii*) Chairman, member or secretary of a large number of scientific advisory boards, committees and organisations set up by the Government of India before partition and later by the Government of Pakistan.

(*viii*) He was also elected (posthumously) a fellow of the University College, London.

Dr. Bashir Ahmad was a scientist of international repute and was highly respected in Pakistan for his sound knowledge and experience in the fields of higher education, scientific research and planning, gained through three decades of close association with research organisations in the Indo-Pakistan subcontinent, the U.K., Germany and the U.S.A. He endeared himself to his colleagues and fellow scientists by his enthusiasm, hard work, and dynamic personality. His approach to the problems of life was characterised by a benevolent humanism. In his presence, the humblest worker as well as the seasoned scientist felt entirely at home. In addition to his scien ific pursuits, he took a keen interest in arts and literature, and was largely responsible for founding the Urdu Academy in Lahore. He was also a keen mountaineer and was President of the Karakorum Mountaineering Club.

The Ismail "Aiwan-i-Science", which is situated in the campus of the West Regional Laboratories, Lahore, and is now nearing completion, owes its existence very largely to the personal efforts of Dr. Bashir Ahmad. This Science House, which is the outcome of close cooperation between scientists and philanthropic citizens, will house a science library, the offices of the scientific societies of the country, and a human relations centre.

In the estimation of all the scientists presens at the international gathering at Peshawar, the untimely demise of Dr. Bashir Ahmad is an irreparable loss to the country, and the Council of Scientific and Industrial Research will be hard put to it to replace him as Director of the West Regional Laboratories. In recognition of the great service rendered by the late Dr. Bashir Ahmad in the cause of science and its propagation in Pakistan, the Council of the Pakistan Association for the Advancement of Science, while deeply mourning his loss, has decided that a Bashir Ahmad Memorial Fund should be established through an appeal to the people, and that this fund should be utilised in a befitting manner to advance the cause for which Dr. Bashir Ahmad lived and gave his life. The President of the Islamic Republic of Pakistan has given his blessing to this proposal, and has graciously agreed to become the Patron of the Fund.

NOTES & NEWS

Fruit Preservation Industry in Pakistan

THE region comprising the former province of the North West Frontier has come to occupy an important position as a fruit growing centre of West Pakistan. In recent years, not only has the area under plantation in this region undergone a rapid and steady increase but new varieties of fruit have been introduced and the indigenous varieties greatly improved in quality.

Despite these improvements, the existing orchards are yet not planted on such a large scale as to make them commercially a worthwhile proposition. This is largely due to the limited nature of the fruit processing industry in the area and the lack of organized research. To meet the latter deficiency a comprehensive research programme has been drawn up for implementation by the Fruit Technology Division of the North Regional Laboratories, the nucleus organization for which was recently established in the University of Peshawar.

Until the Regional Laboratories are constructed and fully equipped, facilities for research will naturally be very limited. As a consequence activities have hitherto been confined to regional surveys with the object of determining the particulars of fruit growing areas, and the state of the existing fruit preservation industry. From the data so far collected it would appear that the area under fruit has increased by about one hundred per cent during the last decade, and is at present estimated to be about 30,000 acres in extent. The annual yield is about 200,000 tons, of varied fruits such as peaches, pears, plums, apricots, grapes, pomegranates, apples, oranges, lemon, lime, quince, guava and dates occurring in diverse varieties.

The examination of five varieties of plums, grown at the Fruit Experimental Station, Tarnab, showed that some of them are well suited for canning and for the manufacture of jams. Four varieties of oranges have also been studied for determining the character of the juice and its keeping qualities. A few varieties of pomegranates have also been tested for the preparation of syrup.

Large scale trials on the utilization of these fruits for different products have not, however, been carried out and will have to wait until the requisite laboratory facilities become available.

A survey of the fruit preservation industry showed that there are at present only two factories, both of which are located near Peshawar. From preliminary observation it appears advantageous to establish medium sized food preservation factories in Kohat District and Swat State as well. A scheme for such a factory in Kohat is being prepared and the necessary data for it collected.

Studies on Goran Bark

Pakistan produces 4,500,000 pieces of cow hide, 9,00,000 pieces of buffalo hides, 55,00,000 pieces of goat skin, 2,200,000 pieces of sheep skin and 2,200,000 pieces of other skins, annually, and has an exportable surplus of these. There are a number of mechanised and cottage tanneries in both wings of Pakistan, which use the vegetable tanning process, so that the requirement of vegetable tanning material for consumption in our tanneries, is considerable It is being met by imports from foreign countries to the extent of about 25 lakhs rupees worth annually.

In the forests of East Pakistan, there are some tannin bearing plants, which are expected to be a possible source material for use by the tanning industry. At present, the most important vegetable tanning material here is the bark of the Goran tree. Unfortunately, the tanning trade is not in favour of using Goran bark, mainly due to the following drawbacks :

(*a*) It produces an ugly red-coloured leather when handled by unexperienced tanners ;

(*b*) There is a tendency to cracyness of the grain of the leathers when the material is used in excess.

Goran (*Ceripos roxburghiana*) is a species of mangrove which grows abundantly in Sundarban Forest of East Pakistan. At present the yield of Goran bark is about 2,500,000 lbs. per annum which can be raised in the future to about 7,500,000 lbs. per annum. (Although Sundarban Forest has been divided due to partition of Bengal, East Pakistan is fortunate in having got most of the Mangrove swamps.) Mangroves

are essentially of tropical growth : the trees grow on sea side swamps, and the bark and wood of the tree contain a high percentage of sodium chloride.

Investigation of the quality of the bark has shown that much improvement can be expected in the bark if the method of collection is improved. Usually the logs after felling are left exposed to moisture and sun for many months before sale, and therefore become dirty and oxidised leading to an even darker colour of the bark. Moreover, the iron instrument used for stripping is also partly responsbile for the objectionable colour of the leather.

Trials in our laboratory on tanning with Goran bark show that the leather is of dark red colour and the grain of the leather is quite rough, which due to careless or imbalanced processing may be cracy. By careful tanning, it has been possible to get a soft mellow leather with Goran bark only, and the colour can be bleached reasonably well. By giving certain special chemical treatment to Goran liquor, a still mellower and softer grained leather has been obtained and a considerable improvement in the colour is observed.

A number of experiments have also been carried out to see the effect of tanning with Goran mixed tannage. While wattle extract alone mixed in suitable proportion shows good improvement of colour, better results can be obtained when myrobolans are included in the blend. Experiments are now in progress to study the effect of different types of syntans to further improve the tanning power of Goran extract. Although a lot of work remains to be done, it can be said, on the basis of the preliminary experiments that Goran bark is going to be an important tanning material in Pakistan in future.

Patent Office Library

At a brief but impressive ceremony, on the 22nd June, 1957, Mr. Abul Mansur Ahmed, the then Central Minister for Commerce and Industries, formally opened the library of the Patent Office at Muhammadi House, McLeod Road, Karachi. The library contains all the Indian patent specifications granted upto the time of partition, abridgements of American, British and Canadian patent specifications, and a good selection of scientific and technical books. It has also two complete sets of Reported Patent Cases covering the British patent law.

In his speech delivered on the occasion, the Minister pointed out the effective part the patent system plays in the industrialization of a country, by granting patents for inventions and by making a vast store of technical information available to the public. He also announced the decision of the Government to open a branch of the Office in East Pakistan.

PATENT NEWS

Patents of the Council of Scientific and Industrial Research

Abridgements

Recovery of coal resins and waxes with simultaneous upranking and partial desulphurisation of the coal. SALIMUZZAMAN SIDDIQUI. (Pakistan Patent No. 105,108 ; Australian Patent No. 166,470 ; British Patent No. 746,486 ; French Patent No. 1,103, 105 ; Indian Patent No. 49,403 ; U.S. Patent No. 2,772,265).—Powdered coal (preferably of a particle size of 20 to 60 mesh B.S.S.) is subjected to the action of superheated steam at subcarbonisation temperatures in the preferred temperature range of 200°C. to 330°C. The coal resins distil over with steam in a depolymerised and chemically modified form along with waxes, and can be collected through fractional condensation. The fractions obtained can be employed in the manufacture of varnishes, enamels and other industrially useful products.

Desulphurisation and upranking of coal.—SALIMUZZMAN SIDDIQUI AND MOHAMMAD NASEEM AHMED. (Pakistan Patent No. 105,109 (Addition to patent No. 105, 108) ; Australian patent No. 166,471; British patent No. 747,730; French patent No. 1,103,105 ; Indian patent No. 49,402).—Alkaline catalysts, such as lime, caustic soda sodium carbonate, magnesium carbonate ammonia and the like, are introduced in the process of superheated steam treatment of powdered coal described in the main patent No. 105108. The preferred particle size of the powdered coals is 30-100 mesh B.S.S. With the help of these catalysts the desulphurisation of coal is facilitated, a comparatively higher degree of desulphurisation being achieved in a given period of superheated treatment, without the recovery of the coal resin being adversely affected. The pyritic sulphur is converted by treatment with superheated steam at about 300°C. into the paramagnetic sulphide of iron which can be magnetically separated, the extent of such separation depending on the state of dispersion of the original pyritic sulphur in the coal body.

Refining of sulphur ore.—IQBAL AHMAD AND KARIMULLAH (Pakistan Specification No. 107149).—Crude sulphur is purified by heating the ore in a saline solution in the presence of a surface active material at 110°C. to 160°C.

Applications Filed

A process for the continuous refining of sulphur ore.—IQBAL AHMAD AND KARIMULLAH. (Pakistan application No. 678, September 19, 1956).

A process for the simultaneous production of refined shark liver oil and vitamin A concentrates along with the recovery of other therapeutically active by-products.—SYED MAHDIHASSAN, MOHAMMAD MOINUDDIN, SYED MAQSOOD ALI AND SYED ABDUL HAQ. (Pakistan application No. 151, February 28, 1957).

An improved clay plaster and bricks.—Abdul HAMID CHOTANI AND MOHAMMAD ASLAM. (Pakistan application No. 182, March 11, 1957).

A process for the production of cottonseed oil based coating compositions.—SALIMUZZAMAN SIDDIQUI AND MOHAMMAD ASLAM. (Pakistan application No. 250, April 5, 1957).

Improvement in or relating to the manufacture of light weight concrete.—MAZHAR MAHMOOD QURASHI, ABDUL HAMID CHOTANI, ABUL KALAM MOHAMMED AHSANULLAH AND MUBARAK AHMAD CHOUDHARI. (Pakistan application No. 312, April 27, 1957).

An improved wood preservaiive.—SALIMUZZAMAN SIDDIQUI, MOHAMMAD ASLAM AND ASHHAD MEHDI. (Pakistan application No. 313, April 27, 1957).

A process for the production of an air entraining agent for cellular concrete.—SALIMUZZAMAN SIDDIQUI, MOHAMMAD ASLAM AND SYED JAMAL QUADIR. (Pakistan application No. 314, April 27, 1957).

Improvements in or relating to emulsion type mimeograph inks and a new stabilizer therefor.—SALIMUZZAMAN SIDDIQUI AND MOHAMMAD ASLAM. (Pakistan application No. 315, April 27, 1957).

A process for the modification of tannin extracts for the manufacture of writing inks.—SALIMUZZAMAN SIDDIQUI, GEORGE HAHN AND RAFIQ AHMAD SIDDIQUI. (Pakistan application No. 366, May 18, 1957).

Improvements in and relating to petrol gas plants.—ABDUL HAMID CHOTANI AND SYED MOHAMMAD ISHAQ ALI. (Pakistan application No. 403, May 29, 1957).

A process for the simultaneous production of refined shark liver oil and vitamin A concentrates along with the recovery of other therapeutically active by-products.—SALIMUZZAMAN SIDDIQUI, SYED MAHDIHASSAN, SYED MAQSOOD ALI AND SYED ABDUL HAQ. (Pakistan application No. 404, May 29, 1957).

A process for the isolation of alkaloids and alkaloidal complexes from the Rauwolfia species of plants. SALIMUZZAMAN SIDDIQUI. (Pakistan application No. 475, June 28, 1957).

A pharmaceutical composition for the treatment of hypertension.—SALIMUZZAMAN SIDDQUI, ROLF DEININGER AND MOHAMMAD ALAUDDIN. (Pakistan application No. 476, June 28, 1957).

CORRIGENDUM

Page 14, second column: *In line* 31 *delete the word* 'the' *and add the words* 'suggest the mode of', *and in line* 32 *add the word* 'that' *after the word* 'molecule'.

Pages 17 to 24: *In the present captions read:*

BADARUDDIN *for* BADRUDDIN

Page 22, Table 7: *In the present caption read:*

SODIUM *for* SGDIUM

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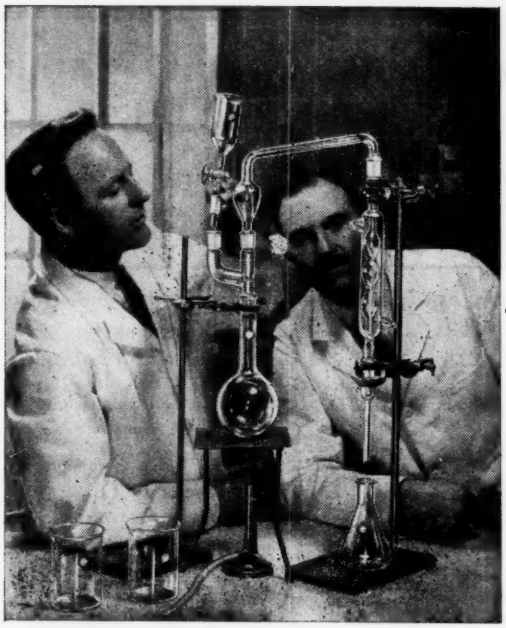

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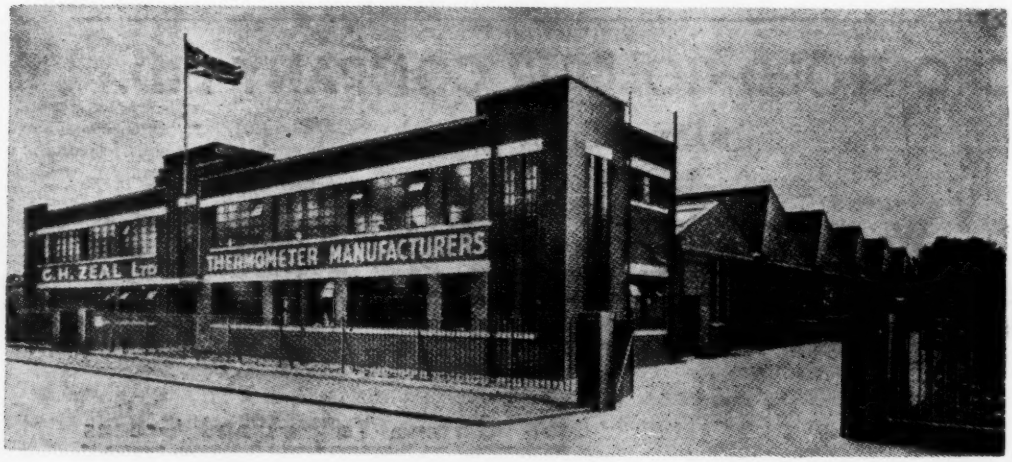

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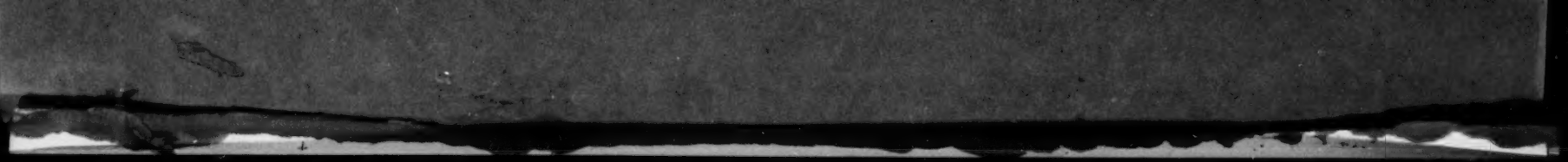
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